Chapter 5 PCBs/trans-Nonachlor in Open-lake Water

5.1 Results

Open-lake samples were collected from 38 sampling stations in Lake Michigan, 2 stations in Green Bay, and 1 station in Lake Huron. A total of 350 samples were collected and analyzed for PCBs and *trans*-nonachlor. Samples were collected as described in Section 2.5.3, by pumping 100 to 1000 L of lake water through a column packed with 250 g of XAD-2®, a macroreticular resin that traps hydrophobic organic contaminants. A "pentaplate" filter was installed in the sampling train in front of the XAD-2® column to collect the particulate matter suspended in the sample. Separate analyses were performed on the XAD-2® resin and the filtered particulates from each sampling effort, yielding results for operationally defined "dissolved" and "particulate" PCBs (Table 5-1) and *trans*-nonachlor (Table 5-2).

The results from two samples collected at Station MB63 in September 1995 are not included in the summary tables. The results for these two samples were several orders of magnitude higher than any other samples collected in the LMMB Study and were removed from consideration based on a consensus of the LMMB modeling team, leaving 348 samples from the rest of the study. Interferences and laboratory accidents further reduced the number of dissolved PCB results to 347 and reduced the number of *trans*-nonachlor results to 341 dissolved results and 347 particulate results.

Of the 38 sampling stations in Lake Michigan, 25 are Figure 5-1. Open-lake Sampling Stations "permanent" monitoring stations used by GLNPO and other investigators for a variety of studies. One additional permanent station is located in Lake Michigan near the mouth of Green Bay (GB100M) and two permanent stations are located in Green Bay itself (GB17 and GB24M). Twelve stations were established for the purposes of the Lake Michigan Mass Balance Study (the "MB" stations in Figure 5-1) and the one station in Lake Huron (LH54M) serves as a means to assess the flux of contaminants from Lake Michigan into Lake Huron. The station locations are

As noted in Chapter 2, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. Battelle Marine Sciences Laboratory determined results for 105 congeners or co-eluting congeners.

For the purposes of this report, we are presenting summaries of the results for the following subset of all of the analytes:

• PCB congener 33

shown in Figure 5-1.

- PCB congener 118
- PCB congener 180
- Total PCBs
- trans-nonachlor

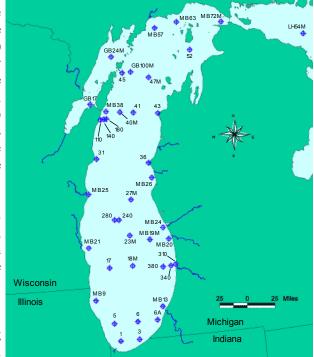


Table 5-1. Numbers of Open-lake Samples Analyzed for Dissolved and Particulate PCB Congeners and Total PCBs

Sampling Station	Sampling Dates	Dissolved PCBs	Particulate PCBs	Total Samples
1	05/10/94 to 10/11/95	5	5	10
3	05/10/94 to 10/13/95	5	5	10
5	05/11/94 to 10/10/95	11	11	22
6	05/09/94 to 10/12/95	6	6	12
6A	05/09/94 to 10/13/95	5	5	10
9	05/11/94 to 10/10/95	6	6	12
13	05/09/94 to 10/13/95	5	5	10
17	05/07/94 to 10/09/95	8	8	16
18M	05/07/94 to 10/09/95	17	17	34
19M	05/05/94 to 10/05/95	11	11	22
20	05/05/94 to 10/06/95	6	6	12
21	05/07/94 to 10/04/95	9	9	18
23M	05/04/94 to 10/03/95	17	17	34
24	05/05/94 to 10/05/95	5	5	10
25	05/03/94 to 09/29/95	6	5	11
26	05/02/94 to 09/27/95	3	4	7
27M	05/02/94 to 09/28/95	16	16	32
31	05/02/94 to 09/28/95	5	5	10
36	05/01/94 to 09/27/95	4	4	8
38	04/28/94 to 09/22/95	6	6	12
40M	04/30/94 to 09/26/95	11	11	22
41	05/01/94 to 09/27/95	9	9	18
43	05/01/94 to 09/26/95	5	5	10
45	04/26/94 to 09/20/95	5	5	10
47M	04/26/94 to 09/20/95	13	13	26
52	04/26/94 to 09/19/95	8	8	16
57	04/25/94 to 09/18/95	5	5	10
63	04/25/94 to 09/18/95	5	5	10
72M	04/25/94 to 09/17/95	8	8	16
110	06/19/94 to 09/24/95	6	6	12
140	04/28/94 to 09/23/95	10	10	20
180	06/18/94 to 09/22/95	11	11	22
240	05/04/94 to 10/02/95	10	11	21
280	05/04/94 to 10/02/95	14	14	28
310	05/06/94 to 10/08/95	7	7	14
340	05/06/94 to 10/07/95	11	11	22
380	05/06/94 to 10/06/95	13	13	26
GB17	04/27/94 to 09/22/95	8	8	16
GB24M	04/27/94 to 09/21/95	10	9	19
GB100M	04/26/94 to 09/20/95	9	10	19
LH54M	04/24/94 to 09/17/95	13	13	26
	Total	347	348	695

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Table 5-2. Number of Open-lake Samples Analyzed for Dissolved and Particulate *trans*-Nonachlor

Sampling Station	Sampling Dates	Dissolved trans-Nonachlor	Particulate <i>trans</i> -Nonachlor	Total Samples
1	05/10/94 to 10/11/95	5	5	10
3	05/10/94 to 10/13/95	5	5	10
5	05/11/94 to 10/10/95	10	11	21
6	05/09/94 to 10/12/95	6	6	12
6A	05/09/94 to 10/13/95	5	5	10
9	05/11/94 to 10/10/95	6	6	12
13	05/09/94 to 10/13/95	5	5	10
17	05/07/94 to 10/09/95	8	8	16
18M	05/07/94 to 10/09/95	16	17	33
19M	05/05/94 to 10/05/95	11	11	22
20	05/05/94 to 10/06/95	5	6	11
21	05/07/94 to 10/04/95	9	9	18
23M	05/04/94 to 10/03/95	17	17	34
24	05/05/94 to 10/05/95	5	5	10
25	05/03/94 to 09/29/95	5	5	10
26	05/02/94 to 09/27/95	3	4	7
27M	05/02/94 to 09/28/95	16	16	32
31	05/02/94 to 09/28/95	5	5	10
36	05/01/94 to 09/27/95	4	4	8
38	04/28/94 to 09/22/95	6	6	12
40M	04/30/94 to 09/26/95	11	11	22
41	05/01/94 to 09/27/95	9	9	18
43	05/01/94 to 09/26/95	5	5	10
45	04/26/94 to 09/20/95	5	5	10
47M	04/26/94 to 09/20/95	13	13	26
52	04/26/94 to 09/19/95	8	8	16
57	04/25/94 to 09/18/95	5	5	10
63	04/25/94 to 09/18/95	5	5	10
72M	04/25/94 to 09/17/95	8	7	15
110	06/19/94 to 09/24/95	6	6	12
140	04/28/94 to 09/23/95	10	10	20
180	06/18/94 to 09/22/95	11	11	22
240	05/04/94 to 10/02/95	10	11	21
280	05/04/94 to 10/02/95	12	14	26
310	05/06/94 to 10/08/95	7	7	14
340	05/06/94 to 10/07/95	11	11	22
380	05/06/94 to 10/06/95	13	13	26
GB17	04/27/94 to 09/22/95	8	8	16
GB24M	04/27/94 to 09/21/95	10	9	19
GB100M	04/26/94 to 09/20/95	9	10	19
LH54M	04/24/94 to 09/17/95	13	13	26
	Total	341	347	688

5.1.1 Temporal Variation

Temporal variation was assessed by examining the mean concentrations of dissolved and particulate total PCBs across seven cruises of the *R/V Lake Guardian* (Figures 5-2 and 5-3). The data from the January 1995 cruise were not included in this assessment because winter lake conditions only permitted the collection of samples at four stations. In general, the mean dissolved and particulate concentrations of total PCBs show little variation over time, with no discernable temporal or seasonal trends. An analysis of variance found no differences between the concentrations by cruise. In the context of a mass balance, the concentrations of PCBs and *trans*-nonachlor in the open lake reflect a large number of inputs, internal processes, and outputs of a complex ecosystem. The observed total PCB concentrations in the open lake over the course of this study may reflect competing temporal trends among those inputs, outputs, and processes. However, the apparent lack of temporal trends shown in these figures is complicated by concerns about contamination of the XAD-2® resin. Those concerns are discussed in detail in Section 5.2.3

Figure 5-2. Dissolved Total PCB by Cruise

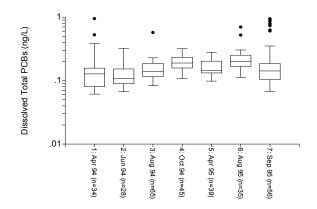
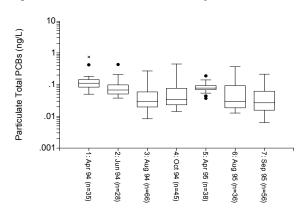


Figure 5-3. Dissolved Total PCB by Cruise



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The Xs represent results beyond 3*IQR from the box. Concentration is plotted on a log scale and the scales for the two figures are different.

5.1.2 Geographical Variation

The concentrations of dissolved and particulate PCBs and *trans*-nonachlor varied by station over the course of the study (Tables 5-3 through 5-12). EPA researchers at the Large Lakes Research Station in Grosse Ile, Michigan, used the data from the LMMB Study to prepare "contour plots" of the lake where similar concentrations of PCBs and *trans*-nonachlor are indicated using a color scale. Examples of such plots are shown in Figures 5-4 to 5-11 for the dissolved and particulate concentrations of PCBs 33, 118, and 180, and *trans*-nonachlor. Similar plots for dissolved total PCBs and particulate total PCBs are shown in Figures 5-12 and 5-13.

The data in these tables and figures include all of the valid data from open lake samples, except the two samples at Station MB63 discussed in Section 5.1. The use and interpretation of the results in these tables and figures is complicated by concerns about contamination of the XAD-2® resin. Those concerns are discussed in detail in Section 5.2.3.

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Table 5-3. Concentrations of Dissolved PCB Congener 33 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00748	0.00392 to 0.0122	0.00304	41	0
3	5	0.00622	0.00418 to 0.00742	0.00137	22	0
5	11	0.0187	0.00217 to 0.0975	0.0303	163	0
6	6	0.0101	0.00349 to 0.0235	0.00750	74	0
6A	5	0.00630	0.00516 to 0.00909	0.00166	26	0
9	6	0.0684	0.00234 to 0.206	0.0987	144	0
13	5	0.00718	0.00567 to 0.00981	0.00164	23	0
17	8	0.00639	0.00358 to 0.00826	0.00159	25	0
18M	17	0.00617	0.00240 to 0.00991	0.00231	37	0
19M	11	0.00624	0.00487 to 0.00958	0.00136	22	0
20	5	0.00749	0.00571 to 0.0120	0.00268	36	0
21	9	0.00660	0.00331 to 0.0152	0.00350	53	0
23M	17	0.0107	0.00400 to 0.0853	0.0193	180	0
24	5	0.00727	0.00585 to 0.0106	0.00202	28	0
25	6	0.00445	0.00302 to 0.00611	0.00127	28	0
26	3	0.00584	0.00451 to 0.00722	0.00136	23	0
27M	16	0.00416	0.00191 to 0.00830	0.00202	49	0
31	5	0.00562	0.00349 to 0.0112	0.00324	58	0
36	4	0.0296	0.00382 to 0.100	0.0472	160	0
38	6	0.00535	0.00398 to 0.00730	0.00112	21	0
40M	10	0.00514	0.00332 to 0.00947	0.00178	35	0
41	9	0.00306	0.00237 to 0.00438	0.000671	22	0
43	5	0.00448	0.00247 to 0.00785	0.00216	48	0
45	5	0.00528	0.00290 to 0.00918	0.00244	46	0
47M	12	0.00460	0.00123 to 0.00700	0.00184	40	0
52	7	0.00510	0.00344 to 0.00658	0.00117	23	0
57	5	0.00374	0.00278 to 0.00459	0.000742	20	0
63	5	0.00338	0.00252 to 0.00499	0.00094	28	0
72M	8	0.00366	0.00270 to 0.00469	0.000785	21	0
110	6	0.00894	0.00277 to 0.0337	0.0121	136	0
140	10	0.00373	0.00 to 0.00530	0.00158	42	10
180	11	0.00717	0.00325 to 0.0335	0.00876	122	0
240	10	0.00496	0.00346 to 0.00763	0.00114	23	0
280	14	0.0307	0.00250 to 0.194	0.0651	212	0
310	7	0.00787	0.00590 to 0.0118	0.00212	27	0
340	11	0.00585	0.00305 to 0.00899	0.00174	30	0
380	13	0.00590	0.00202 to 0.0114	0.00219	37	0
GB17	8	0.0127	0.00287 to 0.0254	0.00709	56	0
GB24M	10	0.00512	0.00335 to 0.00806	0.00154	30	0
GB100M	8	0.00421	0.00228 to 0.00707	0.00170	41	0
LH54M	13	0.00398	0.00116 to 0.0122	0.00270	68	0

Table 5-4. Concentrations of Particulate PCB Congener 33 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00148	0.00 to 0.00530	0.00218	147	20
3	5	0.00113	0.00 to 0.00375	0.00151	133	20
5	11	0.000634	0.00 to 0.00361	0.00100	158	10
6	6	0.000413	0.00 to 0.00133	0.000501	121	33
6A	5	0.00205	0.00 to 0.00770	0.00320	156	20
9	6	0.000694	0.000129 to 0.00126	0.000421	61	0
13	5	0.00208	0.00 to 0.00698	0.00286	137	20
17	8	0.000550	0.00 to 0.00194	0.000619	113	25
18M	17	0.000573	0.00 to 0.00233	0.000788	138	29
19M	11	0.000605	0.00 to 0.00244	0.000898	149	27
20	6	0.00101	0.000193 to 0.00195	0.000694	69	0
21	9	0.000593	0.00 to 0.00158	0.000497	84	11
23M	17	0.000615	0.00 to 0.00382	0.000942	153	18
24	5	0.000793	0.000188 to 0.00225	0.000853	108	0
25	5	0.000676	0.000142 to 0.00157	0.000627	93	0
26	4	0.000910	0.0000872 to 0.00285	0.00131	144	25
27M	16	0.000497	0.00 to 0.00166	0.000519	104	13
31	5	0.000842	0.00 to 0.00290	0.00120	143	20
36	4	0.00476	0.00 to 0.0180	0.00884	185	25
38	6	0.000438	0.00 to 0.00168	0.000633	145	33
40M	11	0.000207	0.00 to 0.000649	0.000258	125	55
41	9	0.000302	0.00 to 0.00202	0.000666	220	67
43	5	0.000740	0.00 to 0.00305	0.00130	175	20
45	5	0.000446	0.000117 to 0.00145	0.000566	127	0
47M	13	0.000360	0.00 to 0.00236	0.000681	189	62
52	8	0.000441	0.00 to 0.00238	0.000798	181	25
57	5	0.000732	0.00 to 0.00332	0.00145	198	60
63	5	0.00123	0.00 to 0.00516	0.00220	178	40
72M	7	0.000112	0.00 to 0.000285	0.000135	121	57
110	6	0.000214	0.00 to 0.000648	0.000238	111	33
140	10	0.000566	0.00 to 0.00268	0.000789	139	30
180	11	0.000351	0.00 to 0.000833	0.000315	90	27
240	11	0.000466	0.00 to 0.00204	0.000615	132	36
280	13	0.000349	0.00 to 0.000890	0.000281	80	23
310	7	0.00331	0.000611 to 0.0100	0.00330	100	0
340	11	0.00147	0.00 to 0.00414	0.00132	90	18
380	13	0.000825	0.00 to 0.00266	0.000692	84	15
GB17	8	0.0283	0.0130 to 0.0578	0.0131	46	0
GB24M	9	0.00108	0.000209 to 0.00340	0.000977	90	0
GB100M	10	0.000237	0.00 to 0.000714	0.000249	105	40
LH54M	13	0.000245	0.00 to 0.00125	0.000377	154	54

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Table 5-5. Concentrations of Dissolved PCB Congener 118 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00117	0.00 to 0.00183	0.000747	64	20
3	5	0.00129	0.00 to 0.00252	0.00109	85	40
5	11	0.00306	0.00 to 0.00974	0.00302	99	18
6	6	0.00227	0.000869 to 0.00407	0.00130	57	0
6A	5	0.000921	0.00 to 0.00250	0.000978	106	60
9	6	0.00356	0.00 to 0.00802	0.00297	84	33
13	5	0.00167	0.000797 to 0.00232	0.000636	38	0
17	8	0.00318	0.00 to 0.0128	0.00405	127	25
18M	17	0.00330	0.00 to 0.0125	0.00331	100	6
19M	11	0.00363	0.000223 to 0.0119	0.00359	99	18
20	5	0.00245	0.00 to 0.00745	0.00305	124	40
21	9	0.00328	0.000858 to 0.0142	0.00426	130	0
23M	17	0.00218	0.000394 to 0.00555	0.00149	69	6
24	5	0.00275	0.00 to 0.00896	0.00362	132	40
25	6	0.00253	0.000616 to 0.00948	0.00346	137	33
26	3	0.000825	0.000377 to 0.00120	0.000417	50	33
27M	16	0.00142	0.000338 to 0.00522	0.00109	77	6
31	5	0.00260	0.00 to 0.0104	0.00439	169	40
36	4	0.00426	0.000273 to 0.0142	0.00663	156	25
38	6	0.00363	0.000216 to 0.0139	0.00520	143	33
40M	10	0.00256	0.0000681 to 0.0115	0.00338	132	40
41	9	0.000788	0.00 to 0.00208	0.000635	81	44
43	5	0.00174	0.000159 to 0.00396	0.00146	84	20
45	5	0.00171	0.000626 to 0.00353	0.00132	77	40
47M	12	0.00258	0.000269 to 0.00994	0.00342	132	33
52	7	0.000790	0.00 to 0.00207	0.000670	85	57
57	5	0.00173	0.000202 to 0.00453	0.00192	111	60
63	5	0.00088	0.00039 to 0.00166	0.00056	63	60
72M	8	0.000760	0.00 to 0.00208	0.000676	89	63
110	6	0.00230	0.000255 to 0.00846	0.00320	139	33
140	10	0.00219	0.0000899 to 0.00912	0.00294	134	30
180	11	0.00265	0.000228 to 0.00991	0.00274	103	18
240	10	0.00254	0.000738 to 0.00823	0.00259	102	0
280	14	0.00420	0.00 to 0.0183	0.00580	138	14
310	7	0.00352	0.00144 to 0.00552	0.00167	47	0
340	11	0.00286	0.00 to 0.00867	0.00268	94	18
380	13	0.00272	0.00 to 0.0111	0.00328	121	15
GB17	8	0.00406	0.00195 to 0.00727	0.00183	45	0
GB24M	10	0.00218	0.000302 to 0.00729	0.00206	94	10
GB100M	8	0.00218	0.000422 to 0.00798	0.00249	114	13
LH54M	13	0.00163	0.0000737 to 0.00947	0.00254	156	38

Table 5-6. Concentrations of Particulate PCB Congener 118 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00252	0.000610 to 0.00730	0.00282	112	0
3	5	0.00223	0.000269 to 0.00683	0.00264	118	20
5	11	0.00195	0.000315 to 0.00450	0.00134	69	0
6	6	0.00203	0.00 to 0.00402	0.00198	98	17
6A	5	0.00358	0.00 to 0.0136	0.00567	158	40
9	6	0.00194	0.000354 to 0.00441	0.00154	79	0
13	5	0.00378	0.00 to 0.0131	0.00537	142	20
17	8	0.00255	0.000111 to 0.00420	0.00176	69	13
18M	17	0.00215	0.00 to 0.0139	0.00376	174	29
19M	11	0.00272	0.0000860 to 0.0124	0.00352	130	9
20	6	0.00307	0.00111 to 0.00504	0.00156	51	0
21	9	0.00275	0.000704 to 0.00816	0.00236	86	0
23M	17	0.00284	0.00 to 0.0129	0.00325	114	12
24	5	0.00245	0.000849 to 0.00510	0.00173	71	0
25	5	0.00172	0.000476 to 0.00288	0.000914	53	0
26	4	0.00218	0.00109 to 0.00352	0.00120	55	0
27M	16	0.00224	0.000109 to 0.00702	0.00224	100	13
31	5	0.00162	0.000527 to 0.00258	0.000934	58	0
36	4	0.00254	0.000722 to 0.00457	0.00177	70	0
38	6	0.00136	0.000543 to 0.00267	0.000841	62	0
40M	11	0.000581	0.00 to 0.00162	0.000494	85	18
41	9	0.000553	0.000229 to 0.000942	0.000300	54	22
43	5	0.00130	0.000407 to 0.00239	0.000957	74	0
45	5	0.00133	0.000450 to 0.00241	0.000777	58	0
47M	13	0.000618	0.00 to 0.00166	0.000556	90	31
52	8	0.00104	0.00 to 0.00270	0.000927	89	13
57	5	0.00114	0.00 to 0.00232	0.00106	93	20
63	5	0.00141	0.00 to 0.002550	0.00118	83	20
72M	7	0.000637	0.00 to 0.00136	0.000495	78	29
110	6	0.00121	0.000398 to 0.00204	0.000723	60	0
140	10	0.00140	0.000267 to 0.00280	0.000988	71	0
180	11	0.00141	0.0000435 to 0.00273	0.00104	74	9
240	11	0.00176	0.0000510 to 0.00368	0.00149	85	18
280	13	0.00214	0.0000664 to 0.00411	0.00148	69	15
310	7	0.0101	0.00240 to 0.0263	0.00852	84	0
340	11	0.00436	0.0000385 to 0.0122	0.00388	89	18
380	13	0.00371	0.0000735 to 0.00660	0.00228	61	8
GB17	8	0.0157	0.00 to 0.0326	0.0116	74	25
GB24M	9	0.00233	0.000283 to 0.00410	0.00121	52	11
GB100M	10	0.00119	0.00 to 0.00226	0.000806	68	10
LH54M	13	0.000839	0.00 to 0.00230	0.000821	98	38

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Table 5-7. Concentrations of Dissolved PCB Congener 180 Measured in Open-lake Samples

Sampling Station	N N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.000340	0.00 to 0.00156	0.000684	201	80
3	5	0.000143	0.00 to 0.00228	0.000208	175	70
5	11	0.00311	0.00 to 0.000747	0.00880	153	89
6	6	0.000400	0.00 to 0.000345	0.000692	133	83
6A	5	0.000371	0.00 to 0.00405	0.000694	208	80
9	6	0.000882	0.00 to 0.000347	0.00191	159	100
13	5	0.000486	0.00 to 0.0295	0.000921	283	64
17	8	0.000383	0.00 to 0.00160	0.000748	187	80
18M	17	0.000258	0.00 to 0.00309	0.000642	223	83
19M	11	0.000314	0.00 to 0.00211	0.000605	190	80
20	5	0.000289	0.00 to 0.000381	0.000411	189	90
21	9	0.000263	0.00 to 0.00211	0.000455	195	75
23M	17	0.000119	0.00 to 0.000563	0.000260	158	91
24	5	0.000757	0.00 to 0.00258	0.00146	249	82
25	6	0.000555	0.00 to 0.000882	0.000855	142	60
26	3	0.000518	0.00 to 0.00139	0.000580	173	78
27M	16	0.000294	0.00 to 0.000891	0.000516	218	88
31	5	0.000535	0.00 to 0.00223	0.00116	154	50
36	4	0.00262	0.00 to 0.0124	0.00481	236	71
38	6	0.0000565	0.00 to 0.00261	0.0000637	217	80
40M	10	0.000107	0.00 to 0.00144	0.000181	259	82
41	9	0.000165	0.00 to 0.00982	0.000252	183	50
43	5	0.000228	0.00 to 0.000128	0.000316	113	100
45	5	0.000148	0.00 to 0.00346	0.000145	218	69
47M	12	0.0000981	0.00 to 0.000518	0.000131	170	80
52	7	0.000151	0.00 to 0.000630	0.000246	138	60
57	5	0.000858	0.00 to 0.000291	0.00179	98	100
63	5	0.000183	0.00 to 0.00060	0.00024	133	100
72M	8	0.0000796	0.00 to 0.0479	0.000127	172	57
110	6	0.000556	0.00 to 0.000458	0.00124	146	80
140	10	0.0000667	0.00 to 0.00177	0.000126	173	67
180	11	0.000116	0.00 to 0.00476	0.000183	217	67
240	10	0.000414	0.00 to 0.00196	0.000724	192	73
280	14	0.00145	0.00 to 0.00334	0.00343	193	60
310	7	0.000712	0.00 to 0.00114	0.00151	112	33
340	11	0.000170	0.00 to 0.00209	0.000441	175	69
380	13	0.000445	0.00 to 0.00404	0.000970	212	71
GB17	8	0.00109	0.00 to 0.00699	0.00240	220	63
GB24M	10	0.000296	0.00 to 0.00186	0.000568	192	80
GB100M	8	0.000137	0.00 to 0.000282	0.000117	85	100
LH54M	13	0.000121	0.00 to 0.000527	0.000175	144	85

Table 5-8. Concentrations of Particulate PCB Congener 180 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.000974	0.00 to 0.00248	0.00128	132	40
3	5	0.000943	0.00 to 0.00364	0.00121	170	55
5	11	0.000807	0.00 to 0.00103	0.000343	300	89
6	6	0.00115	0.00 to 0.00168	0.000488	145	46
6A	5	0.00160	0.00 to 0.00288	0.00123	173	40
9	6	0.000654	0.00 to 0.00125	0.000485	181	71
13	5	0.00162	0.00 to 0.00246	0.000864	107	36
17	8	0.00111	0.00 to 0.00568	0.00238	149	40
18M	17	0.000929	0.00 to 0.000577	0.000283	128	50
19M	11	0.00123	0.00 to 0.00531	0.00219	135	40
20	6	0.00178	0.00 to 0.00168	0.000534	146	50
21	9	0.00110	0.00 to 0.00278	0.00104	93	38
23M	17	0.00112	0.00 to 0.000954	0.000373	135	55
24	5	0.00143	0.00 to 0.00547	0.00151	162	47
25	5	0.000415	0.0000299 to 0.00371	0.00144	81	17
26	4	0.000919	0.00 to 0.00241	0.000886	80	22
27M	16	0.000729	0.00 to 0.00407	0.00122	109	29
31	5	0.000553	0.00 to 0.00183	0.000800	193	60
36	4	0.00115	0.00 to 0.00183	0.000663	88	31
38	6	0.000329	0.00 to 0.00161	0.000664	120	40
40M	11	0.000200	0.00 to 0.00586	0.00189	86	18
41	9	0.000114	0.00 to 0.00332	0.00157	137	50
43	5	0.000581	0.00 to 0.00197	0.000805	245	83
45	5	0.000552	0.00 to 0.00477	0.00139	77	15
47M	13	0.000336	0.00 to 0.00139	0.000455	227	82
52	8	0.000532	0.00 to 0.00232	0.00100	173	60
57	5	0.000709	0.00 to 0.00164	0.000710	129	40
63	5	0.00093	0.00 to 0.00207	0.000913	98	60
72M	7	0.000268	0.00 to 0.00207	0.000833	115	29
110	6	0.000221	0.00 to 0.00276	0.00119	126	40
140	10	0.000365	0.00 to 0.00276	0.00135	118	50
180	11	0.000277	0.00 to 0.00142	0.000511	78	17
240	11	0.000708	0.00 to 0.00477	0.00167	135	45
280	13	0.000751	0.00 to 0.00516	0.00218	152	20
310	7	0.00431	0.00 to 0.00296	0.00140	153	50
340	11	0.00219	0.00 to 0.00307	0.000902	124	38
380	13	0.00180	0.000761 to 0.0117	0.00399	93	0
GB17	8	0.00644	0.00415 to 0.0142	0.00332	52	0
GB24M	9	0.000627	0.00 to 0.00238	0.000840	134	44
GB100M	10	0.000593	0.00 to 0.00199	0.000730	123	50
LH54M	13	0.000314	0.00 to 0.00111	0.000428	136	62

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Table 5-9. Concentrations of Dissolved Total PCBs Measured in Open-lake Samples

Sampling Station	N N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)
1	5	0.172	0.0796 to 0.227	0.0616	36
3	5	0.187	0.107 to 0.137	0.0566	13
5	11	0.303	0.0758 to 0.574	0.282	85
6	6	0.168	0.0864 to 0.165	0.0447	26
6A	5	0.169	0.138 to 0.200	0.0271	16
9	6	0.364	0.0613 to 0.898	0.360	99
13	5	0.199	0.0713 to 0.865	0.0493	93
17	8	0.180	0.103 to 0.788	0.0285	102
18M	17	0.166	0.0932 to 0.528	0.0636	73
19M	11	0.169	0.142 to 0.219	0.0450	16
20	6	0.181	0.0791 to 0.248	0.106	39
21	9	0.189	0.0669 to 0.304	0.0600	38
23M	17	0.174	0.0996 to 0.232	0.0652	27
24	5	0.207	0.00 to 0.319	0.0594	59
25	6	0.140	0.101 to 0.352	0.0557	38
26	3	0.121	0.170 to 0.312	0.0151	29
27M	16	0.131	0.0789 to 0.274	0.0474	40
31	5	0.144	0.0722 to 0.253	0.0531	36
36	4	0.299	0.185 to 0.949	0.292	75
38	6	0.185	0.123 to 0.243	0.104	23
40M	11	0.145	0.113 to 0.384	0.0720	56
41	9	0.104	0.128 to 0.270	0.0216	26
43	5	0.142	0.00 to 0.269	0.0550	50
45	5	0.232	0.0692 to 0.126	0.197	21
47M	13	0.133	0.0806 to 0.216	0.0761	39
52	8	0.115	0.00 to 0.272	0.0503	57
57	5	0.121	0.00 to 0.167	0.0318	44
63	5	0.107	0.0731 to 0.156	0.3058	31
72M	8	0.118	0.0682 to 0.204	0.0500	42
110	6	0.257	0.108 to 0.243	0.262	30
140	10	0.178	0.100 to 0.209	0.130	27
180	11	0.164	0.157 to 0.280	0.0641	25
240	10	0.159	0.0920 to 0.249	0.0629	32
280	14	0.245	0.100 to 0.247	0.239	40
310	7	0.373	0.0673 to 0.944	0.280	97
340	11	0.179	0.0992 to 0.219	0.0421	37
380	13	0.182	0.116 to 0.734	0.0465	98
GB17	8	0.653	0.290 to 1.52	0.420	64
GB24M	10	0.166	0.0844 to 0.247	0.0602	36
GB100M	9	0.289	0.00 to 0.634	0.256	89
LH54M	13	0.129	0.0526 to 0.209	0.0556	43

Table 5-10. Concentrations of Particulate Total PCBs Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)
1	5	0.100	0.0334 to 0.270	0.102	101
3	5	0.0830	0.0344 to 0.144	0.0867	65
5	11	0.0699	0.0259 to 0.0877	0.0490	51
6	6	0.0563	0.0159 to 0.137	0.0445	92
6A	5	0.140	0.0217 to 0.449	0.174	124
9	6	0.0728	0.0222 to 0.126	0.0349	48
13	5	0.138	0.0196 to 0.170	0.165	70
17	8	0.0707	0.0161 to 0.0774	0.0416	56
18M	17	0.0652	0.0224 to 0.0996	0.0712	54
19M	11	0.0757	0.0131 to 0.124	0.0783	59
20	6	0.103	0.0141 to 0.0814	0.0573	52
21	9	0.0910	0.0113 to 0.264	0.0479	109
23M	17	0.0754	0.00836 to 0.269	0.0620	103
24	5	0.0870	0.0355 to 0.181	0.0653	55
25	5	0.0522	0.0129 to 0.245	0.0203	82
26	4	0.0843	0.0279 to 0.181	0.0548	75
27M	16	0.0630	0.0104 to 0.115	0.0434	71
31	5	0.0619	0.0103 to 0.152	0.0354	69
36	4	0.150	0.0776 to 0.744	0.183	80
38	6	0.0575	0.0127 to 0.365	0.0385	79
40M	11	0.0271	0.0211 to 0.122	0.0132	67
41	9	0.0307	0.0151 to 0.181	0.0198	53
43	5	0.0549	0.0144 to 0.0541	0.0443	49
45	5	0.0527	0.0115 to 0.0734	0.0269	64
47M	13	0.0312	0.0165 to 0.123	0.0239	81
52	8	0.0416	0.00637 to 0.0894	0.0333	77
57	5	0.0558	0.0157 to 0.112	0.0512	80
63	5	0.0654	0.0203 to 0.159	0.055	84
72M	8	0.0275	0.00 to 0.0663	0.0205	75
110	6	0.0424	0.0141 to 0.234	0.0236	104
140	10	0.0547	0.0129 to 0.109	0.0297	79
180	11	0.0500	0.0110 to 0.420	0.0261	120
240	11	0.0590	0.0306 to 0.200	0.0418	53
280	14	0.0581	0.0199 to 0.0681	0.0358	39
310	7	0.297	0.00 to 0.101	0.237	62
340	11	0.134	0.0232 to 0.108	0.106	57
380	13	0.103	0.0253 to 0.421	0.0549	122
GB17	8	1.02	0.468 to 2.30	0.553	54
GB24M	9	0.0810	0.0402 to 0.137	0.0341	42
GB100M	10	0.0459	0.0105 to 0.109	0.0312	68
LH54M	13	0.0379	0.00976 to 0.103	0.0268	71

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Table 5-11. Concentrations of Dissolved *trans*-Nonachlor Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	ns-Nonachior Measure Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00507	0.00227 to 0.00863	0.00303	60	0
3	5	0.00545	0.00 to 0.0119	0.00296	59	10
5	10	0.0111	0.000359 to 0.0124	0.0118	76	11
6	6	0.00870	0.00 to 0.0102	0.00656	77	23
6A	5	0.00429	0.00 to 0.00594	0.00302	115	40
9	6	0.00430	0.00 to 0.00590	0.00405	63	25
13	5	0.00548	0.00160 to 0.0392	0.00338	106	0
17	8	0.0236	0.000807 to 0.00786	0.0494	70	20
18M	16	0.00659	0.00124 to 0.0165	0.00393	71	17
19M	11	0.00773	0.000917 to 0.00888	0.00613	62	20
20	5	0.00450	0.00 to 0.0463	0.00423	156	30
21	9	0.00366	0.00 to 0.145	0.00467	209	13
23M	17	0.00368	0.00 to 0.0102	0.00367	68	18
24	5	0.00579	0.00 to 0.0131	0.00258	60	19
25	5	0.00478	0.00 to 0.00984	0.00361	94	40
26	3	0.00440	0.00 to 0.0150	0.00467	127	44
27M	16	0.00524	0.00 to 0.0108	0.00432	100	41
31	5	0.00402	0.00118 to 0.0101	0.00366	76	20
36	4	0.00228	0.00 to 0.0145	0.00457	66	8
38	6	0.00432	0.00 to 0.00962	0.00467	91	20
40M	11	0.00433	0.00 to 0.0138	0.00376	88	27
41	9	0.00475	0.00 to 0.00913	0.00361	200	75
43	5	0.00289	0.00 to 0.0127	0.00251	108	33
45	5	0.00397	0.000786 to 0.0129	0.000926	63	8
47M	13	0.00388	0.00 to 0.00998	0.00300	87	27
52	8	0.00375	0.000239 to 0.00650	0.00261	87	40
57	5	0.00232	0.00296 to 0.00542	0.00266	23	0
63	5	0.00296	0.00152 to 0.00494	0.00135	46	20
72M	8	0.00330	0.00152 to 0.176	0.00207	238	0
110	6	0.00728	0.00108 to 0.00832	0.00516	54	20
140	10	0.00869	0.00 to 0.0193	0.0136	75	17
180	11	0.00481	0.00 to 0.00932	0.00328	94	33
240	10	0.00627	0.00 to 0.0169	0.00368	79	18
280	12	0.00637	0.00146 to 0.00789	0.00422	45	0
310	7	0.00530	0.00 to 0.00930	0.00184	106	33
340	11	0.00551	0.00 to 0.0139	0.00483	82	19
380	13	0.00604	0.00253 to 0.00749	0.00383	35	0
GB17	8	0.00560	0.00145 to 0.0159	0.00497	89	0
GB24M	10	0.00348	0.00 to 0.00733	0.00213	61	10
GB100M	9	0.00531	0.00 to 0.0113	0.00347	65	22
LH54M	13	0.00876	0.00 to 0.0774	0.0210	239	46

Table 5-12. Concentrations of Particulate *trans*-Nonachlor Measured in Open-lake Samples

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Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.0026	0.000509 to 0.00844	0.0033	127	0
3	5	0.0012	0.000365 to 0.00771	0.0011	96	9
5	11	0.0027	0.000109 to 0.00575	0.0029	116	22
6	6	0.0013	0.00 to 0.00644	0.0017	133	31
6A	5	0.0040	0.000396 to 0.00687	0.0023	103	0
9	6	0.0025	0.000531 to 0.00298	0.0019	60	0
13	5	0.0014	0.00 to 0.0104	0.0010	105	18
17	8	0.0015	0.00121 to 0.00621	0.0008	57	0
18M	17	0.0018	0.000571 to 0.00636	0.0024	98	0
19M	11	0.0012	0.00 to 0.00245	0.0011	72	20
20	6	0.0021	0.000552 to 0.00652	0.0013	79	0
21	9	0.0027	0.000912 to 0.00342	0.0022	52	0
23M	17	0.0021	0.00 to 0.00475	0.0016	82	18
24	5	0.0027	0.00 to 0.00844	0.0021	138	29
25	5	0.0014	0.000773 to 0.00403	0.0007	64	0
26	4	0.0024	0.00 to 0.00665	0.0027	80	11
27M	16	0.0022	0.000391 to 0.00622	0.0021	76	0
31	5	0.0016	0.000468 to 0.00217	0.0008	51	0
36	4	0.0031	0.000180 to 0.00657	0.0024	84	14
38	6	0.0025	0.000423 to 0.00228	0.0024	46	20
40M	11	0.0011	0.00 to 0.00889	0.0010	95	9
41	9	0.0015	0.00102 to 0.00639	0.0018	79	0
43	5	0.0023	0.000604 to 0.00683	0.0020	96	0
45	5	0.0026	0.000452 to 0.00679	0.0023	84	0
47M	13	0.0014	0.00 to 0.00344	0.0018	88	27
52	8	0.0017	0.000887 to 0.00583	0.0016	90	0
57	5	0.0025	0.000264 to 0.00596	0.0026	90	20
63	5	0.00226	0.00 to 0.00542	0.0022	97	20
72M	7	0.0016	0.00 to 0.00542	0.0009	109	14
110	6	0.0023	0.00 to 0.00261	0.0022	91	20
140	10	0.0029	0.00 to 0.00474	0.0023	132	33
180	11	0.0017	0.000508 to 0.00583	0.0014	75	0
240	11	0.0023	0.00 to 0.00409	0.0022	93	18
280	14	0.0025	0.000501 to 0.00570	0.0021	77	0
310	7	0.0030	0.000918 to 0.00643	0.0022	112	0
340	11	0.0031	0.00 to 0.00791	0.0029	96	13
380	13	0.0025	0.000887 to 0.00761	0.0021	75	0
GB17	8	0.0037	0.00119 to 0.00893	0.0025	66	0
GB24M	9	0.0020	0.000253 to 0.00355	0.0011	56	11
GB100M	10	0.0019	0.00 to 0.00580	0.0020	102	20
LH54M	13	0.0011	0.00 to 0.00307	0.0009	87	38
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Figures 5-4 to 5-13 illustrate the concentrations of PCBs 33, 118, 180, total PCBs, and *trans*-nonachlor in the dissolved and particulate samples collected over the course of the LMMB Study.

Note: The color scales used in these contour plots vary with each plot. Therefore, although the red end of the visible spectrum always represents higher concentrations than the violet end of the spectrum, the absolute magnitude represented by each color differs with the contaminant and the phase (dissolved versus particulate). Each plot includes a concentration scale and readers are advised to consult those scales carefully when comparing the plots.

The plots of the dissolved PCB congeners (Figures 5-4 to 5-6) indicate that the concentrations of these contaminants are generally lowest in the far northern areas of the lake that are removed from urban influences. The highest dissolved concentrations generally are found in the southwest area of the lake, centered around Station 9, which lies between the urban areas of Chicago and Milwaukee. The dissolved PCB concentrations suggest that there may be a point source at Waukegan Harbor, Illinois. The concentrations of these dissolved contaminants show some increase in Green Bay, with dissolved PCB 118 concentrations highest overall at Station GB 17, near the discharge of the Fox River. (The apparent decrease in concentrations of these contaminants from Station GB 17 to the head of Green Bay likely is a function of the lack of a sampling station further up Green Bay).

The plots of the particulate PCB congeners (Figures 5-7 to 5-9) illustrate the importance of contaminant sources in Green Bay. The particulate PCB concentrations are highest in Green Bay, at Station GB 17, with much lower particulate PCB concentrations in the remainder of the lake. The particulate concentrations of PCBs 118 and 180 show a slight increase in the southeast portion of the lake, in the area between the mouths of the St. Joseph and Kalamazoo Rivers. However, the concentrations of particulate PCBs 118 and 180 in that area are still 2 to 5 times lower than in the upper reaches of Green Bay.

The patterns of dissolved concentrations of *trans*-nonachlor (Figure 5-10) are similar to those of the dissolved PCB congeners, with an apparent increase in concentration in the southwest portion of the lake, near Chicago. The increase in concentration on the western shore of the lake seen in Figure 5-10 suggests that the Sturgeon Bay ship canal, which connects lower Green Bay with this portion of Lake Michigan, results in the transfer of water containing dissolved *trans*-nonachlor from Green Bay into Lake Michigan.

The particulate concentrations of *trans*-nonachlor (Figure 5-11) are similar to those of the particulate PCB congeners, with the highest concentrations in Green Bay, near Station GB 17. However, particulate *trans*-nonachlor concentrations appear to be increased in areas of the lake adjacent to most of the major urban areas around the lake. However, similar increases occur near the discharges of the Manistique and Pere Marquette Rivers, which are not associated with urban areas, suggesting that the increases near the urban area may be a function of river-borne sources of particulate *trans*-nonachlor, including resuspension of contaminated sediments. The particulate *trans*-nonachlor results also suggest the transfer of contaminants from lower Green Bay to Lake Michigan via the Sturgeon Bay ship canal.

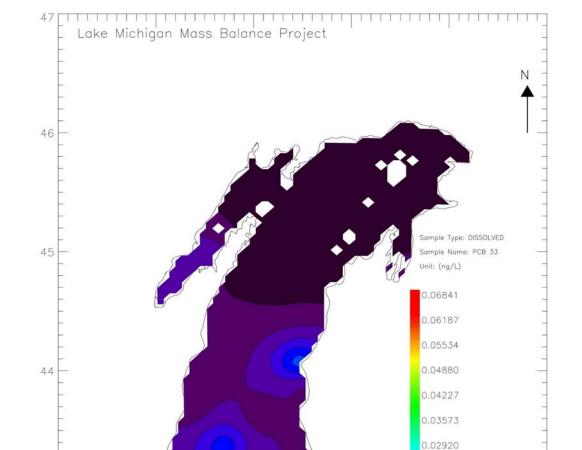
The plots of dissolved and particulate total PCBs (Figures 5-12 and 5-13) illustrate the importance of the sources of these contaminants in Green Bay. The dissolved total PCB concentrations are highest in Green Bay. However, the dissolved total PCB concentrations in the lower portion of Lake Michigan are higher than in the northern portion of the lake, with an apparent hot spot near Chicago. The particulate total PCB concentrations are also highest in Green Bay and lower throughout the main portion of the lake, with a slight increase in the southeast portion of the lake, similar to the particulate PCB 118 and 180 results. The dissolved and particulate PCB results show less indication of the transfer of contaminants from lower Green Bay to Lake Michigan via the Sturgeon Bay ship canal than the results for *trans*-nonachlor, with increases for the congeners reported here evident only for dissolved PCB 118 and dissolved total PCBs.

43

42

-89

-88



0.02266

0.01613 0.00959 0.00306

4/24/94 - 10/13/95

OM - 300M

Survey Date:

-86

Sample Depths:

Figure 5-4. Concentrations of Dissolved PCB Congener 33 Measured in Open-lake Samples

5-16 April 2004

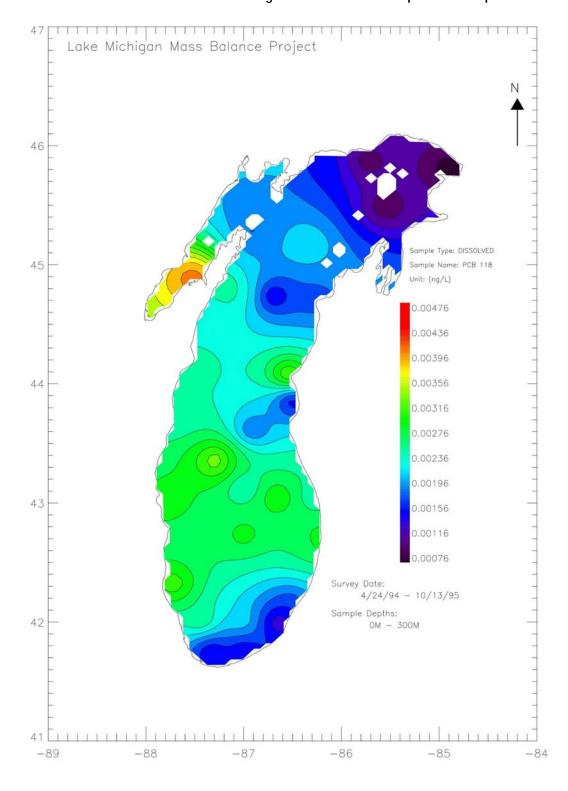
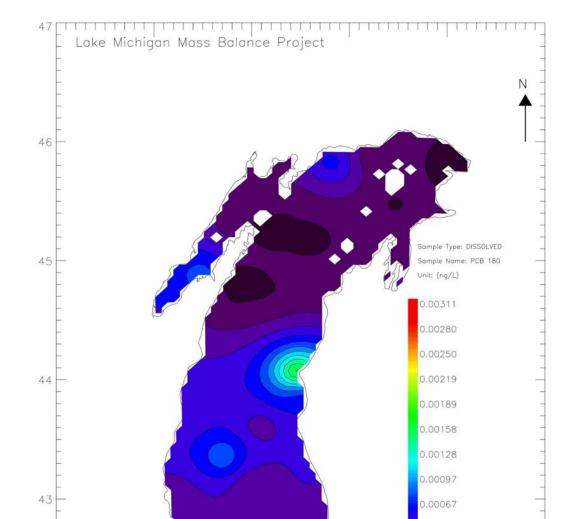


Figure 5-5. Concentrations of Dissolved PCB Congener 118 Measured in Open-lake Samples

42

-89

-88



0.00036

-84

4/24/94 - 10/13/95

OM - 300M

Survey Date:

-86

Sample Depths:

Figure 5-6. Concentrations of Dissolved PCB Congener 180 Measured in Open-lake Samples

5-18 April 2004

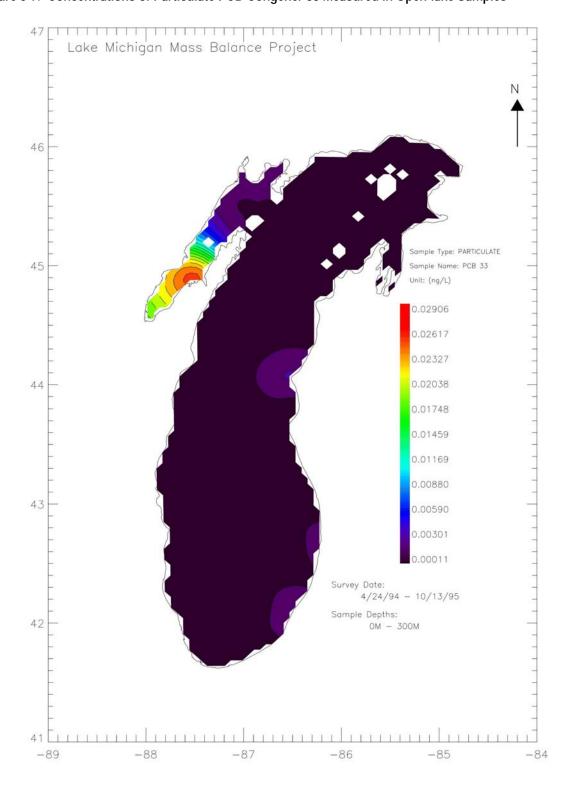


Figure 5-7. Concentrations of Particulate PCB Congener 33 Measured in Open-lake Samples

-89

-88

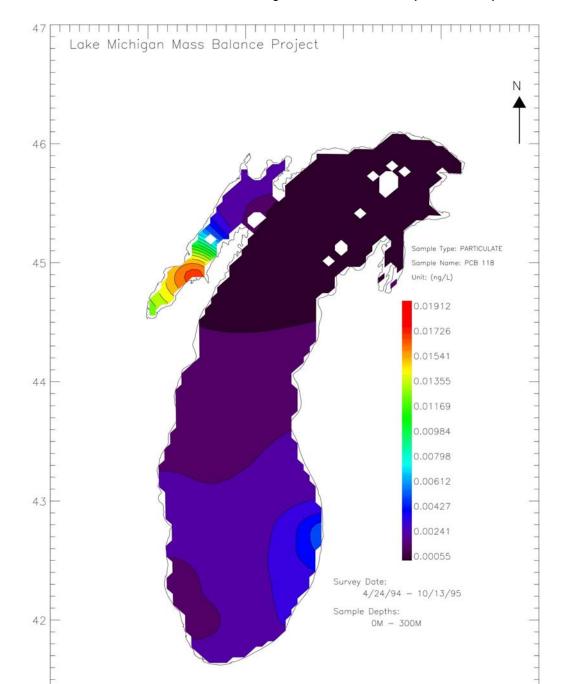


Figure 5-8. Concentrations of Particulate PCB Congener 118 Measured in Open-lake Samples

5-20 April 2004

-86

-84

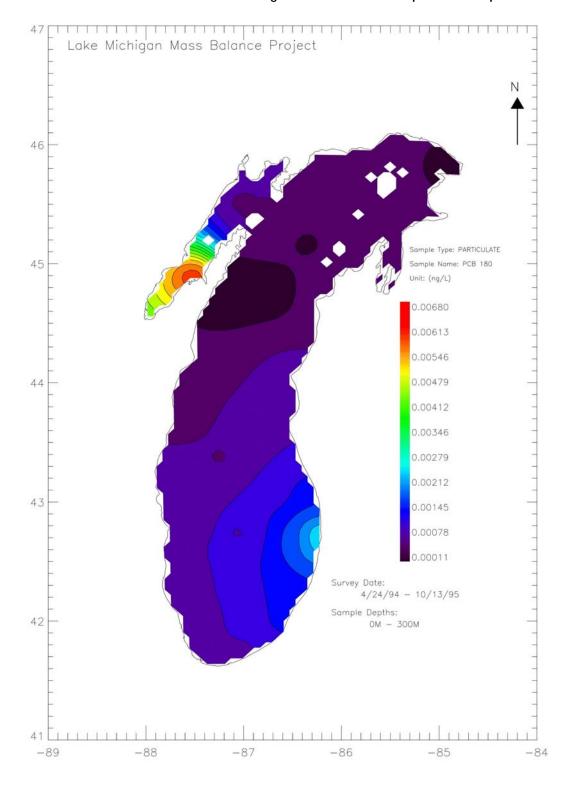
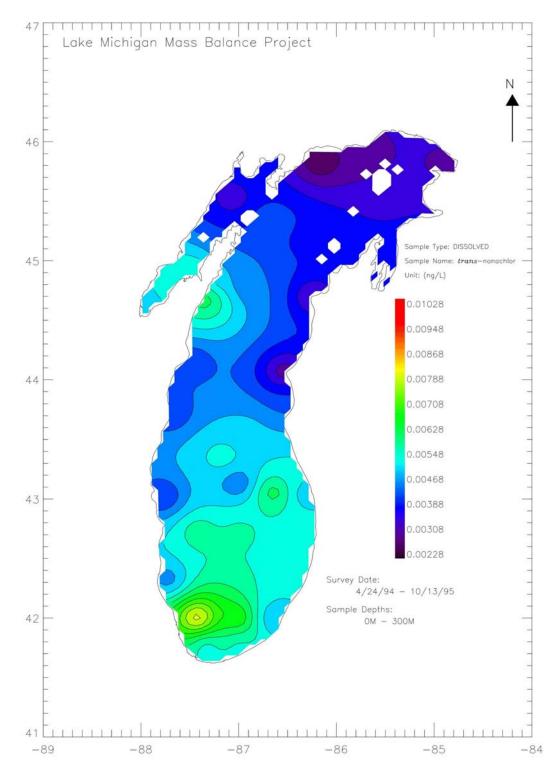


Figure 5-9. Concentrations of Particulate PCB Congener 180 Measured in Open-lake Samples

Figure 5-10. Concentrations of Dissolved *trans*-Nonachlor Measured in Open-lake Samples



5-22 April 2004

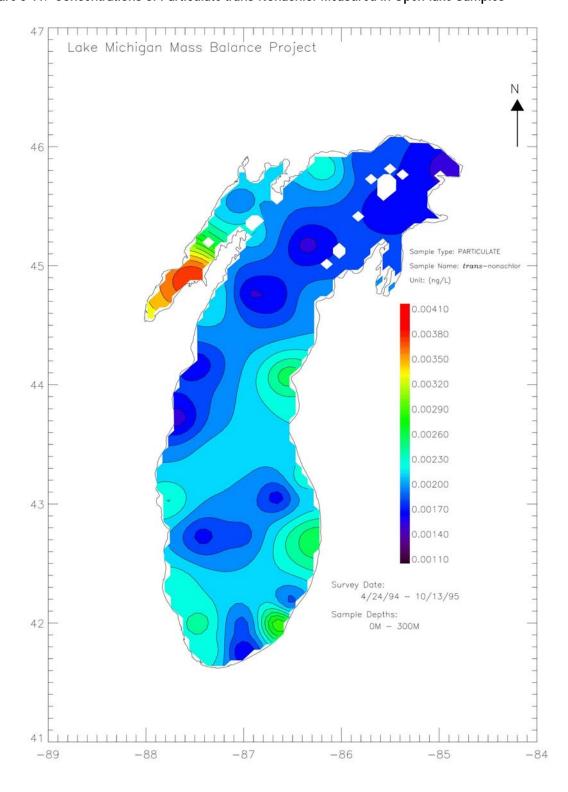
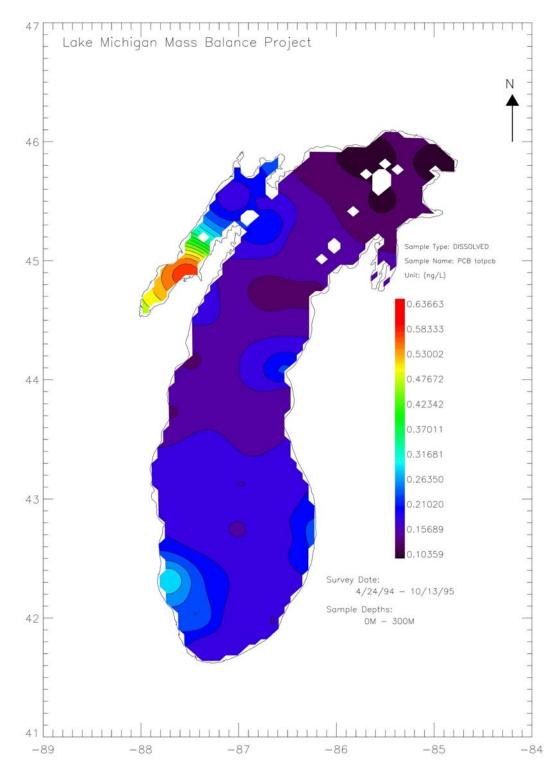


Figure 5-11. Concentrations of Particulate trans-Nonachlor Measured in Open-lake Samples

Figure 5-12. Concentrations of Dissolved Total PCBs Measured in Open-lake Samples



5-24 April 2004

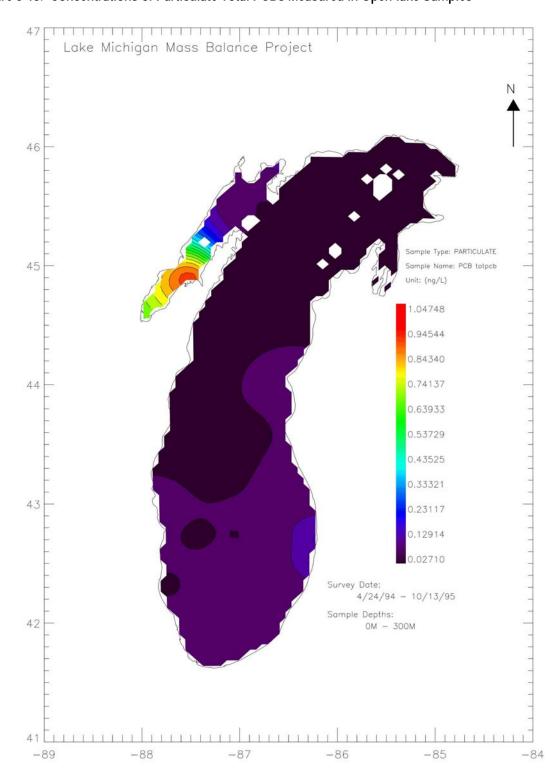


Figure 5-13. Concentrations of Particulate Total PCBs Measured in Open-lake Samples

5.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in the *Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of data quality issues for the open lake PCBs and *trans*-nonachlor data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.5, because data comparability was important to the successful development of the mass balance model, the PIs used similar sample collection, extraction, and analysis methods for the PCB and *trans*-nonachlor monitoring in this study.

5.2.1 Sample Collection

During examination of the field collection records for field duplicates, it was discovered that some field duplicates were not actually collected at the same time as the field sample due to equipment mobilization. Samples collected within five minutes of each other were considered field duplicates (FD1), and if more than five minutes elapsed, the samples were considered sequential field duplicates (SFD1). Separate labeling of these data points as FD1 and SFD1 was done in order to assess if precision differed based on the elapsed time.

5.2.2 Data Assessments

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 5-13 provides a summary of flags applied to the open lake PCB and *trans*-nonachlor data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7.

PIs used surrogate spikes to monitor the bias of the analytical procedure. The PCB results were corrected for the recoveries of the surrogates. The *trans*-nonachlor results were *not* surrogate-corrected. Only 1% of each of the open-lake particulate results for PCBs 33, 118, and 180, and *trans*-nonachlor were qualified because of surrogate recovery problems (Table 5-13). For the dissolved PCB samples from the open lake, 3 to 5% of the results for PCBs 33, 118, and 180 were qualified for surrogate recovery problems (Tables 5-13), while 19% of the dissolved *trans*-nonachlor results were qualified.

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Laboratory matrix spike samples also were used to monitor the bias of the analytical procedure. The results for the matrix spike samples were compared to the MQO for spike recoveries (50 - 125%). Analytical results associated with matrix spike samples with recoveries below the MQO limits were flagged with failed matrix spike and low bias flags, and results associated with matrix spike samples that had recoveries higher than the MQO limits were flagged with failed matrix spike and high bias flags. Analytical results were considered invalid and flagged as such when the analyte was undetected and recoveries for associated matrix spike samples were less than 10%. None of the open-lake particulate *trans*-nonachlor results or PCB 33, 118, or 180 results failed the matrix spike MQOs. However, 8% of the open-lake dissolved PCB 33 results, 14% of the open-lake dissolved PCB 118 results, and 71% of the open-lake dissolved *trans*-nonachlor results were flagged as failing the matrix spike MQOs. A maximum of 1% of the samples were flagged as invalid.

Field blanks were collected for PCBs and *trans*-nonachlor. Field blanks were to be collected at a frequency of 5%. Due to the limited availability of samplers and resin, the actual frequency was only 3.5% When field blank contamination was greater than 3.3 times the method detection limit, all of the associated results were flagged with the failed field blank sample code (FFR). Field blanks were not collected at all stations, so potential station-specific contamination associated with these sites cannot be evaluated. However, contamination associated with sampling equipment, collection, processing, shipping, storing, and analysis can be evaluated based on the field blanks collected throughout the study. Large percentages of samples were associated with field blanks in which PCBs 33, 118, or 180, or *trans*-nonachlor were reported above the sample-specific detection limit (Table 5-13). This issue is discussed in greater detail in Section 5.2.3.

Trip blanks were collected for PCBs and *trans*-nonachlor. Trip blanks were to be collected at a frequency of 5%. Due to the limited availability of samplers and resin, the actual frequency was only 2.2%. As with the field blanks, large percentages of samples were associated with a trip blank in which PCBs 33, 118, or 180, or *trans*-nonachlor were reported above the sample-specific detection limit (Table 5-13). This issue is discussed in greater detail in Section 5.2.3.

Field duplicates were to be collected at a frequency of 5%. Duplicate samples collected within 5 minutes of each other were considered field duplicates. However, an examination of the field collection records indicated that some of the planned field duplicates were not collected within that 5-minute time frame as a result of problems with equipment mobilization or the time required to pump the sample through the filter and resin cartridge. Those "duplicates" that were collected more than 5 minutes apart were considered "sequential field duplicates" and the data were labeled accordingly (e.g., SDF1 vs. FD1). Combining the field duplicates and sequential field duplicates, the actual rate of collection of duplicates was 7.6%.

The results from the original field sample and the associated duplicate were compared on the basis of the relative percent difference (RPD). The RPD value for each PCB congener and *trans*-nonachlor was compared to the MQO for field duplicate precision. None of the particulate PCB results were qualified because of the field duplicate precision (FFD) concerns (Table 5-13). Only 2% of the particulate *trans*-nonachlor results were so qualified. The percentage of dissolved PCB and *trans*-nonachlor results that were qualified because of field duplicate precision concerns ranged from 0.3% to 2%.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate pairs. Table 5-14 provides a summary of data quality assessments for several of these attributes for the open-lake PCB and *trans*-nonachlor data.

Because the relative variability of most measurement techniques increases as one approaches the detection limit of the technique, the assessment of the field duplicate results were divided into two concentration regimes. One measure of system precision was calculated for those field duplicate results that were less than 5 times the sample-specific detection limit (SSDL) of the analyte, and a separate measure was calculated for those field duplicate results that were greater than 5 times the SSDL. None of the open lake particulate sample field duplicate pairs contained *trans*-nonachlor concentrations above 5 times the SSDL.

The precision of the particulate field duplicate results above 5 times the SSDL ranged from approximately 5 to 11% for the PCB congeners (Table 5-14), while the precision of the particulate field duplicate results below 5 times the SSDL ranged from approximately 23% to 55%.

None of the field duplicate pairs for dissolved samples contained PCB 180 above 5 times the SSDL, and the precision of the dissolved field duplicate results for PCBs 33 and 118, and *trans*-nonachlor above the SSDL ranged from approximately 17% to 36% (Table 5-14).

Analytical bias was assessed using the results from matrix spike samples. The mean recoveries were very good for the particulate-phase PCBs and *trans*-nonachlor, ranging from 88.8% to 105% for the analytes in Table 5-14. These results demonstrate that the analytical techniques applied to the field samples introduced little or no bias into most of the results, and only a slight low bias was introduced into the particulate PCB 118 results.

The matrix spike recoveries of the dissolved analytes were considerably more varied than the particulate results. The recoveries of dissolved PCBs 33 and 180 were very good to excellent, at 80.9% and 109%, respectively. However, the dissolved PCB 118 results indicate a significant high bias, with a mean recovery of 157%, while the dissolved *trans*-nonachlor recoveries average only 33.7%, indicating a significant low bias.

Analytical sensitivity was assessed on the basis of the percentage of study samples that were reported with concentrations below the sample-specific detection limit (SSDL). The sensitivity varied by congener for the PCBs, partly as a function of the analytical instrumentation and its response to the individual congeners.

The three PCB congeners and *trans*-nonachlor were not detected in substantial portions (1 - 55%) of the dissolved and particulate samples from the open lake ("UND" flag in Table 5-13). These analytes were detected below the sample-specific detection limits in substantial portions (1 - 23%) of the samples as well ("MDL" flag in Table 5-13). For the three congeners listed in Table 5-13, the percentage of the dissolved samples with results reported below the sample-specific detection limits increases (i.e., 10, 18, and 23%) with the congener number (e.g., with molecular weight), suggesting that solubility may play a role in the distribution.

The percentages of *trans*-nonachlor results that were not detected or detected below the sample-specific detection limits (Table 5-13) generally fell between the same percentages for the three PCB congeners, and were most similar to the percentages for PCB 118 (e.g., 6 - 12% for *trans*-nonachlor and 5 - 18% for PCB 118).

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Table 5-13. Summary of Routine Field Sample Flags Applied to Select PCB Congeners and trans-Nonachlor in Open-lake Samples

	Fraction	Flags									
Analyte		Sensitivity		Contamination		Precision	Bias				
		MDL	UND	FFR	FFT	FFD	FSS	FMS	LOB	HIB	INV
PCB 33 -	Dissolved	0	1% (2)	85% (297)	59% (206)	1% (2)	5% (16)	8% (29)	0	68% (238)	1% (4)
348 Dissolved 349 Particulate	Particulate	1% (5)	24% (85)	29% (101)	41% (142)	0	1% (4)	0	0	19% (65)	0.3% (1)
PCB 118 -	Dissolved	18% (63)	5% (19)	57% (200)	77% (269)	0.3% (1)	3% (10)	14% (48)	0	57% (197)	1% (4)
348 Dissolved 349 Particulate	Particulate	8% (28)	5% (18)	30% (104)	48% (169)	0	1% (4)	0	0	25% (86)	0.3% (1)
PCB 180 -	Dissolved	23% (79)	55% (190)	53% (183)	38% (131)	1% (3)	3% (10)	0	0	33% (115)	1% (4)
348 Dissolved 349 Particulate	Particulate	3% (12)	39% (135)	20% (71)	14% (48)	0	1% (4)	0	0	9% (33)	0.3% (1)
trans-Nonachlor -	Dissolved	8% (29)	12% (42)	35% (119)	56% (193)	2% (6)	19% (66)	71% (244)	5% (16)	11% (37)	0
343 Dissolved 349 Particulate	Particulate	6% (22)	6% (20)	21% (73)	48% (169)	2% (6)	1% (2)	0	0	7% (26)	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

- MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
- UND = Analyte not detected (Analyte produced no instrument response above noise.)
- FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
- FFT = A trip blank associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.
- FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
- HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
- INV = Invalid

Table 5-14. Data Quality Assessment for Select PCB Congeners and *trans*-Nonachlor in Open-lake Water Samples

Analyte/Number	Davamatan	Number of	Assessment		
Field Samples	Parameter	Dissolved	Particulate	Dissolved	Particulate
PCB 33 - 344 Dissolved 348 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	8 field duplicate pairs	7 field duplicate pairs	55.9%	23.6%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	19 field duplicate pairs	11 field duplicate pairs	17.1%	11.3%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	22 matrix spikes	80.9%	97.6%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	0.3%	25.9%
PCB 118 - 344 Dissolved 348 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	21 field duplicate pairs	8 field duplicate pairs	30.4%	18.2%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	4 field duplicate pairs	13 field duplicate pairs	35.6%	4.96%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	22 matrix spikes	157%	88.8%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	23.0%	13.2%
PCB 180 - 344 Dissolved 348 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	10 field duplicate pairs	6 field duplicate pairs	77.4%	54.9%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	0 field duplicate pairs	12 field duplicate pairs		8.98%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	22 matrix spikes	109%	105%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	77.3%	42.2%
trans-Nonachlor - 343 Dissolved 349 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	23 field duplicate pairs	22 field duplicate pairs	41.0%	36.7%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	1 field duplicate pair	0 field duplicate pairs	17.8%	-
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	22 matrix spikes	33.7%	95.1%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	20.7%	12.0%

As noted in Section 2.6.4, the laboratory did not obtain separate cleanup fractions containing the PCBs and *trans*-nonachlor, but analyzed the sample extracts on two dissimilar GC columns (DB-5 and DB-1701). While the DB-1701 column provided clear chromatographic separation of any *trans*-nonachlor in the sample, this analyte coeluted with PCB 99 on the DB-5 column. As a result of the potential coelution, the reported concentrations of PCB 99 in open-lake samples are probably biased by any *trans*-nonachlor present in the samples.

5.2.3 Evaluation of Blanks

Because PCBs are a ubiquitous contaminant, both in the environment and in environmental testing laboratories, the LMMB Study design included a wide range of types of blanks that were designed to identify many of the potential sources of PCB contamination that might be encountered during the study. Contamination of the samples from other sources was a particular concern because the study attempted to investigate the very low concentrations present in the open lake. When the data were examined, a large number of open-lake PCB sample results (20 - 90%) in the LMMB Study were flagged as being associated with one or more blanks that exhibited signs of contamination.

The data presented in this report thus far include all of the sample results except those flagged as invalid. Samples that were flagged with blank contamination were included in the analyses, and as a result, the estimates of mean concentrations may be biased due to contributions from the various blanks. An evaluation of the blank contaminants was conducted to examine the impacts of these contaminants on the results and conclusions by comparing several alternative approach to flagging and treating sample results.

The reported concentrations of PCBs in the open lake were evaluated with regard to the results of the three types of routine blanks that were prepared for the study. Blanks are important to consider when estimating concentrations of PCB congeners in this study for several reasons including:

- Blank contamination is typical for PCB sampling and analysis, especially for low concentrations of PCB congeners that are close to the detection limit of the analytical method,
- Blank contamination affected a significant number of field samples results collected in the LMMB Study, and
- The analytical laboratory changed its resin cleaning procedures in the middle of the study to comply with a revised criteria for "clean" resin set by GLNPO.

Mean concentrations of open lake PCB congeners were calculated in two ways: using all the LMMB data, and using only those data that were not affected by contamination of the field reagent blank, the laboratory dry blank, or the laboratory reagent blank. For the purposes of this evaluation, a field sample result was considered unaffected by blank contamination if the results of all of the associated blank samples were less than 1/3 of the concentration reported in the field sample.

The criteria for the evaluation were based on the measurement quality objectives (MQOs) established by the principal investigators for open lake PCBs, when possible, because the PIs are most knowledgeable about the performance of their sampling and analytical method.

Table 5-15 provides criteria used to evaluate whether to include a sample result in the estimation of the mean concentrations in the open lake. The approach taken in this evaluation was conservative, in that it was designed to leave as many samples as possible in the estimation of the mean. This evaluation did not consider the effects of the field trip blanks on the sample results for several reasons. First, there were fewer field trip blanks than the other types of blanks. Therefore, there is concern that the results for a given field trip blank may not be as representative of the actual sample collection procedures as other types of blanks. Secondly, the potential contamination illustrated by the field trip blank also could be

evaluated using the field reagent blank results, because the field reagent blank should theoretically capture most of the same sources of contamination.

In addition to the blank considerations listed in Table 5-15, data also were excluded if they were flagged "Invalid" in the database. The invalid flag indicates that the PI and the QC coordinator deemed the data to be unusable for any purpose.

All sample results were included as reported by the PI in the estimate of the mean. If the PI reported a result as zero, then the zero was included in the estimate. A zero result should be interpreted as a concentration that is below the sample-specific detection limit for that sample. In addition, the results that were reported as a value below the sample-specific detection limit also were included in the estimate. These results were flagged in the database with the "MDL" flag and should be interpreted as a concentration that is below the sample-specific detection limit.

Table 5-15. Criteria Used to Evaluate Data to be Included in the Estimation of the Mean Concentrations of PCB Congeners

Quality Control Consideration	Criteria	Rationale				
Blanks, including: • field reagent blanks, • lab dry blanks ¹ , and • lab reagent blanks. ¹	Exclude the sample result when any of the three associated blanks has a result that is greater than 1/3 of the concentration in	When a sample is associated with a blank that has greater than 1/3 of the concentration in the sample result, the result is likely to be biased high and contamination may be a significant portion of the concentration reported in the sample. The multiplier of 1/3 is based on the MQOs				
l	the sample	established by the PI for several blank types.				

¹Lab dry blanks and lab reagent blanks were reported in mass units because there is no actual volume of "sample" pumped through the filter and resin column. The sample results were compared to the results for these two types of blanks by converting the sample results to mass units as well.

The estimation of the mean concentration of each PCB in the open lake was complicated by the use of detection limits that are specific to each sample, rather than using one detection limit for each congener across all lake samples. The sample-specific detection limits take into account the actual volume of lake water pumped through the filter and resin column, which may differ between samples.

There are several approaches that may be used to estimate the mean concentration of each PCB congener in the open-lake samples. One common approach is to substitute the sample-specific detection limit for any result below that limit and use the result as reported for any result above the sample-specific detection limit. However, that approach introduces a high bias into the mean concentration because no result used in the mean will ever be less than the detection limit for that sample. Another common approach is to use the concentrations as reported by the investigator. This approach recognizes that the actual concentrations in the samples may range from zero to the sample-specific detection limit. The modelers using the LMMB data are using the results as reported, including the values reported by the PIs as zero or below the sample-specific detection limit. Therefore, this same approach was used to estimate the mean concentrations for this evaluation.

The mean concentrations for the three PCB congeners are presented in Table 5-16 in four ways, using:

- 1. All data except those flagged invalid in the database,
- 2. Only data without associated blank failures as described in Table 5-15,
- 3. Only data without associated blank failures as described in Table 5-15 for 1994, and
- 4. Only data without associated blank failures as described in Table 5-15 for 1995.

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The differentiation between the 1994 and 1995 data was made because GLNPO lowered the acceptable level of PCBs that could be in the XAD-2® resin and particulate collection filters at the beginning of 1995 and the PIs responded by changing their cleaning procedures. The standard deviation, the concentration range, and the mean sample-specific detection limit are presented in Table 5-16 for the three congeners.

Table 5-16. Comparison of Summary Statistics for LMMB Open-lake PCB Congener Results after Removal of

Sample Results associated with Contaminated Blanks

Analyte	Fraction	Data Included in Mean ¹	N	Mean (pg/L)	SD (pg/L)	Range (pg/L)	Mean SSDL (pg/L)
PCB 33		All data	303	9.15	23.16	0.00 - 205.62	0.578
	Discolude	Data Without Blank Failures	128	8.70	22.27	0.00 - 193.50	0.591
	Dissolved	1994 Data Without Blank Failures	64	5.92	1.60	0.00 - 11.78	0.637
		1995 Data Without Blank Failures	64	11.47	31.33	2.37 - 193.50	0.545
	Particulate	All data	306	0.77	1.54	0.00 - 18.01	0.108
		Data Without Blank Failures	216	0.78	1.79	0.00 - 18.01	0.106
		1994 Data Without Blank Failures	112	1.13	2.36	0.00 - 18.01	0.127
		1995 Data Without Blank Failures	104	0.41	0.63	0.00 - 3.89	0.084
PCB 118	Dissolved	All data	303	2.46	3.01	0.00 - 18.33	0.788
		Data Without Blank Failures	213	3.04	3.30	0.00 - 18.33	0.778
		1994 Data Without Blank Failures	132	3.76	3.32	0.00 - 15.53	0.798
		1995 Data Without Blank Failures	81	1.87	2.94	0.00 - 18.33	0.746
	Particulate	All data	306	2.24	2.88	0.00 - 26.26	0.252
		Data Without Blank Failures	277	2.44	2.96	0.00 - 26.26	0.253
		1994 Data Without Blank Failures	161	2.49	3.26	0.00 - 26.26	0.295
		1995 Data Without Blank Failures	116	2.36	2.48	0.00 - 15.23	0.196
PCB 180	Dissolved	All data	303	0.49	2.03	0.00 - 29.53	0.388
		Data Without Blank Failures	189	0.32	2.45	0.00 - 29.53	0.385
		1994 Data Without Blank Failures	104	0.02	0.06	0.00 - 0.31	0.392
		1995 Data Without Blank Failures	85	0.70	3.62	0.00 - 29.53	0.376
	Particulate	All data	306	0.94	1.40	0.00 - 11.72	0.155
		Data Without Blank Failures	289	0.97	1.44	0.00 - 11.72	0.157
		1994 Data Without Blank Failures	172	1.08	1.61	0.00 - 11.72	0.181
		1995 Data Without Blank Failures	117	0.81	1.13	0.00 - 6.15	0.122

Figures 5-14 to 5-16 provide a graphical display of the means presented in Table 5-16, along with the standard error of each mean (i.e., the standard deviation divided by the square root of the number of observations in each mean), and the mean sample-specific detection limit (SSDL) for the congener.

The four bars in each graph above represent the mean concentrations of the analyte derived from: all data, all data without the samples associated with contaminated blanks, all data from 1994 without samples associated with contaminated blanks, and all data from 1995 without samples associated with contaminated blanks. The y-axis units are the mean concentration of the PCB congener in ng/L. The narrow vertical lines represent ± 1 standard error around the mean concentration. The horizontal line across each graph is the approximate position of the mean sample-specific detection limit (SSDL) for the results from all of the samples for that congener and phase. Note that the vertical scale use for the y-axis differs from congener to congener, based on the observed range of mean concentrations.

The results for dissolved PCB 33 and PCB 180 illustrate the potential for high bias in the mean concentrations derived from all of the data. For both of these congeners, the mean dissolved concentration decreases slightly when the data associated with the contaminated blanks are removed (e.g., the second bar in each graph labeled "data without QC failures"). In contrast, the results for dissolved PCB 118 and the particulate fraction for all three congeners show an *increase* in the mean concentration when the data associated with the contaminated blanks are removed.

The effect of the change in the acceptance criteria for the XAD-2[®] resin between 1994 and 1995 is not consistent across the dissolved congeners. For PCB 118, the 1995 mean concentration of samples without QC failures is about half of the 1994 mean concentration. However, for dissolved PCB 33, the trend is exactly opposite, with the 1995 mean concentration approximately twice the 1994 mean concentration. For dissolved PCB 180, the 1995 mean is actually 35 times higher than the 1994 mean.

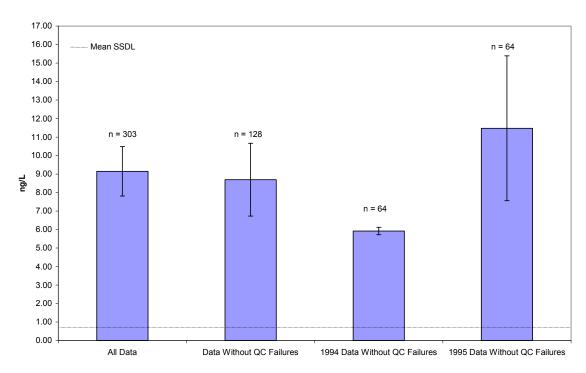
For the particulate sample results, the mean concentrations were lower in 1995 for PCBs 33, 118, and 180. This suggests that the contribution of the blanks to the particulate results may have been less in the 1995 data then in the 1994 data.

The data for the mean SSDL for each congener and fraction also illustrate a significant aspect of the situation. For dissolved PCB 33, the mean sample results, regardless of QC failures, are 7 to 10 times higher than the mean SSDL value. For dissolved PCB 118, the ratio drops to 2 to 4 times the SSDL, and the error bars for the mean dissolved PCB 180 encompass the mean SSDL for three of the four bar graphs. For the particulate PCB results, the mean concentrations of all three congeners are at least five times higher than the mean SSDL values. These results illustrate the congener-specific difficulties in measuring open-lake concentrations that are near or below the capabilities of the analytical techniques.

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Figure 5-14. Summary Statistics for LMMB Open-lake PCB 33 Results after Removal of Sample Results associated with Contaminated Blanks





Particulate PCB 33

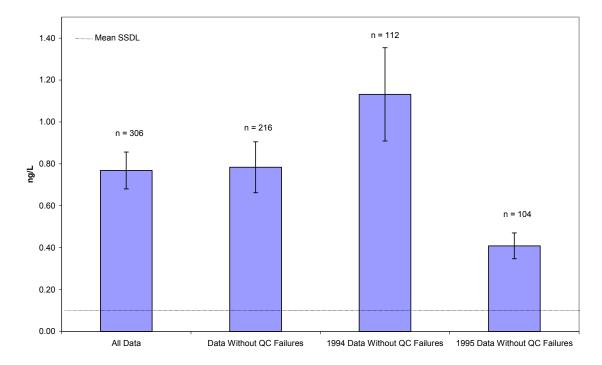
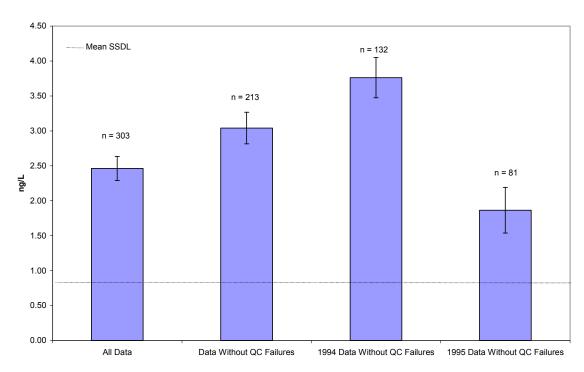
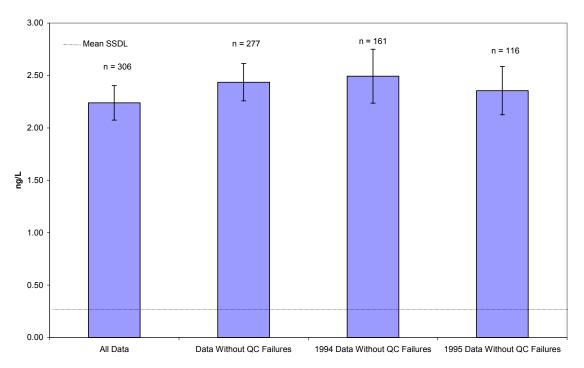


Figure 5-15. Summary Statistics for LMMB Open-lake PCB 118 Results after Removal of Sample Results associated with Contaminated Blanks

Dissolved PCB 118



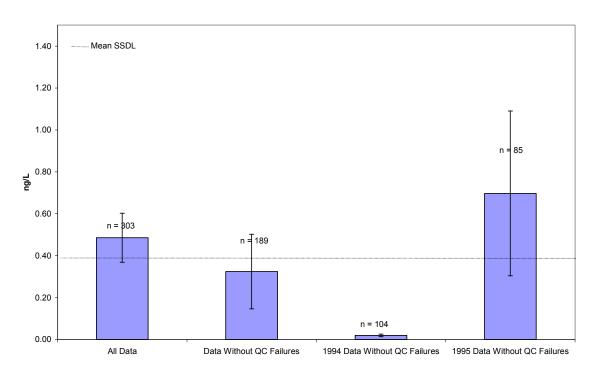
Particulate PCB 118



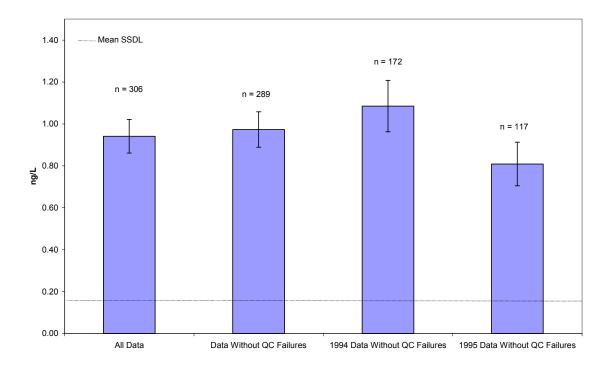
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Figure 5-16. Summary Statistics for LMMB Open-lake PCB 180 Results after Removal of Sample Results associated with Contaminated Blanks

Dissolved PCB 180



Particulate PCB 180



5.3 Data Interpretation

The LMMB Study resulted in one of the largest collections of PCB and *trans*-nonachlor data ever produced for any of the Great Lakes. The data for PCBs and *trans*-nonachlor from the LMMB Study indicate that the concentrations of individual PCB congeners and *trans*-nonachlor vary among the stations in the open lake, In addition, the concentrations of the congeners differ, both within a station, as well as across the stations.

5.3.1 Comparison to Historical Studies

The magnitude of the LMMB data set makes it difficult to find comparable historical results that are useful for comparisons. Even where data are available from other investigators for the same analytes, the potential differences in spatial and temporal coverage present concerns that are further complicated by the likely differences in the sampling and analytical procedures.

Three historical data sets have been identified by EPA's Large Lakes Research Station as relevant to such comparisons. Swackhamer and Armstrong (1987) collected PCB data during September 1980 under a project partially supported by USEPA Cooperative Agreement CR807836. Filkins *et al.* (1983), at the Cranbrook Institute, collected PCB data during September 1981 under a project supported by USEPA Cooperative Agreement CR810232. Pearson *et al.* (1996) collected PCB data during September 1991 under a project supported by GLNPO Grant No. GL995233.

These historical data represent the "total PCB" concentration in each sample, without regard for the dissolved or particulate fraction, and without distinguishing among the PCB congeners. Therefore, the historical results can only be compared to the sum of the dissolved and particulate PCB results from the LMMB Study. Figures 5-17 to 5-20 present the results from the three historical studies and the LMMB results for samples collected in September 1995. Figure 5-20 presents the summary plot for total PCBs for the entire LMMB data set. As with the earlier contour plots, note that the concentrations scales differ among the four plots. The data from the three historical studies represent samples collected in the top 30 meters of the lake, while the LMMB data include samples collected at greater depths as well. Additional comparisons could be made using only the LMMB results for samples collected in the top 30 meters of the lake. However, such plots were not available at the time of this report.

Swackhamer and Armstrong (1987) collected 45-L water samples from 19 stations in the open lake. The water samples were filtered through glass-fiber filters on board the R/V Roger R. Simons. The filtrates were passed through glass columns containing XAD-2[®] resin. The filter and the XAD-2[®] resin were extracted separately, and the extracts were analyzed by GC/ECD. Total PCB concentrations were determined by comparison to standards of Aroclor mixtures, as well as through the use of standards for some individual PCB congeners.

The data from September 1980 (Swackhamer and Armstrong, 1987, Figure 5-17) ranged from 0.4 to 7.9 ng/L, with a mean concentration in the open lake of 1.8 ng/L. The total PCB concentration in central portion of Lake Michigan is between 1.2 and 1.6 ng/L, with lower concentrations (< 0.8 ng/L) in the extreme northern portion of the lake, and with concentrations as high as 6 to 8 ng/L near the shore in the lower portion, close to major urban areas.

Filkins *et al.*, (1983) collected approximately 120 L of water from a depth of 4 m at four stations in Lake Michigan, as part of a larger study involving 21 stations in all five Great Lakes. The water samples were collected as 3-L aliquots placed in multiple 1-gallon glass bottles. Methylene chloride was added to each bottle, and the bottles were shaken for 3 minutes. After standing for two hours to allow the solvent and water sample to separate, the methylene chloride was removed from each bottle and stored. The extracts

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from the individual bottles were concentrated and combined into a single final extract that was analyzed by GC/ECD. Total PCB concentrations were determined by comparison to specific PCB congeners identified in a mixed Aroclor standard. Filkins *et al.* (1983) provide data on the percentage of the sample result represented by the method blanks associated with each sample. For the four Lake Michigan samples, the associated blanks represent 14 to 122% of the associated sample result.

The data from September 1981 (Filkins, *et al.*, 1983, Figure 5-18) represent the results from only four samples in all of Lake Michigan. The total PCB concentrations in this study ranged from about 0.25 ng/L in the extreme northern portion and the central portion of the lake, to about 0.31 ng/L at a station near Chicago, with a similar concentration found at the mouth of Green Bay.

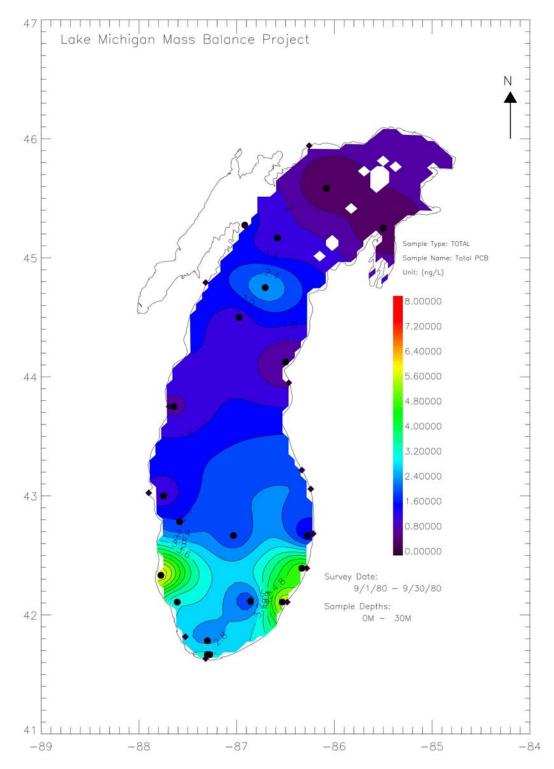
Pearson *et al.* (1996) collected approximately 100 L of water at each of 11 stations in Lake Michigan abroad the *R/V Lake Guardian*. Samples were filtered through glass fiber filters on board the ship. The filtrate was collected in 70-L stainless steel tanks and returned to the laboratory were it was extracted using a continuous flow liquid-liquid Goulden large-volume extraction device. Particulate and dissolved extracts were analyzed separately, using GC/ECD. The total PCB concentrations were calculated by summing the results determined for individual congeners using an internal standard method and surrogate correction.

The data from September 1991 (Pearson, *et al.*, 1996, Figure 5-19) includes significantly more stations than in 1981. Total PCB concentrations range from 0.34 to 1.7 ng/L, with a lake-wide mean concentration of 0.64 ng/L. Because the congener distribution patterns at two of the stations differed from those at the other nine stations, Pearson *et al.* also calculated a mean concentration of 0.47 ng/L for the nine stations alone. The northern portions of the lake contain approximately 0.5 ng/L of total PCBs, with concentrations of about 1 ng/L in the southern portion of the lake. The hot spot apparent in the southern portion of the lake has a maximum concentration of 1.7 ng/L. Overall, the total PCB concentrations are lower than in 1980 throughout the lake.

The LMMB data from September 1995 (Figure 5-20) suggest further decreases in the total PCB concentrations lake-wide since 1991. These data suggest that the concentrations in the northern portion of the lake are less than 0.15 ng/L. A hot spot appears in the southern portion of the lake with a maximum concentration of about 0.7 ng/L, roughly half the concentration is a similar hotspot found in 1991. Thus, the September 1995 total PCB data suggest a drop in concentration of about 50% from the 1991 results, and a drop of almost an order of magnitude from the 1980 results. In addition, the data in Figure 5-21 for the entire LMMB Study suggest that the results from September 1995 (Figure 5-20) are not unusual for the period of the LMMB Study itself.

Historical data for *trans*-nonachlor were not available, so no inferences can be made regarding changes in the concentrations of this contaminant in Lake Michigan.

 $Figure \ 5\text{-}17. \ \ Concentrations \ of \ Total \ PCBs \ Measured \ in \ Open-lake \ Samples \ in \ September \ 1980$



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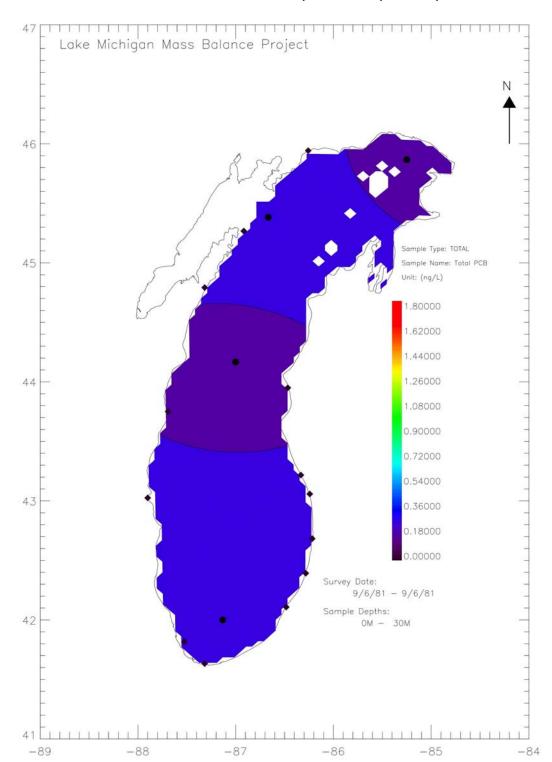
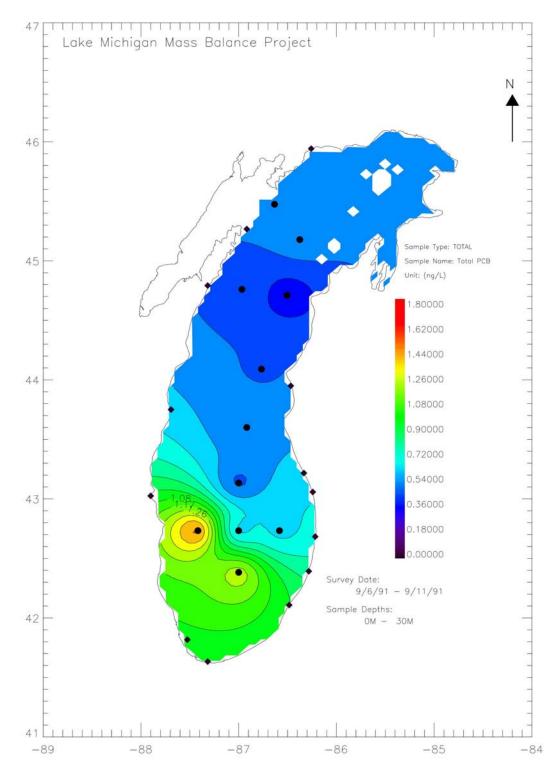


Figure 5-18. Concentrations of Total PCBs Measured in Open-lake Samples in September 1981

Figure 5-19. Concentrations of Total PCBs Measured in Open-lake Samples in September 1991



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Figure 5-20 Concentrations of Total PCBs Measured in LMMB Open-lake Samples in September 1995

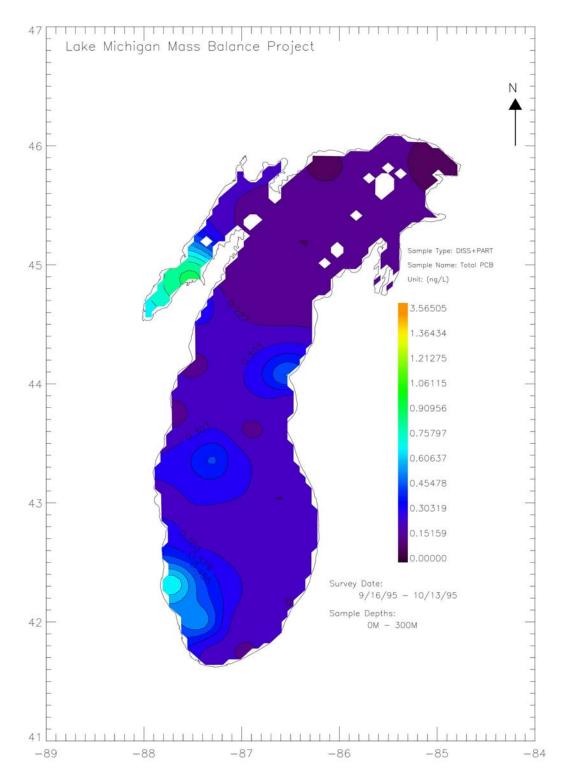
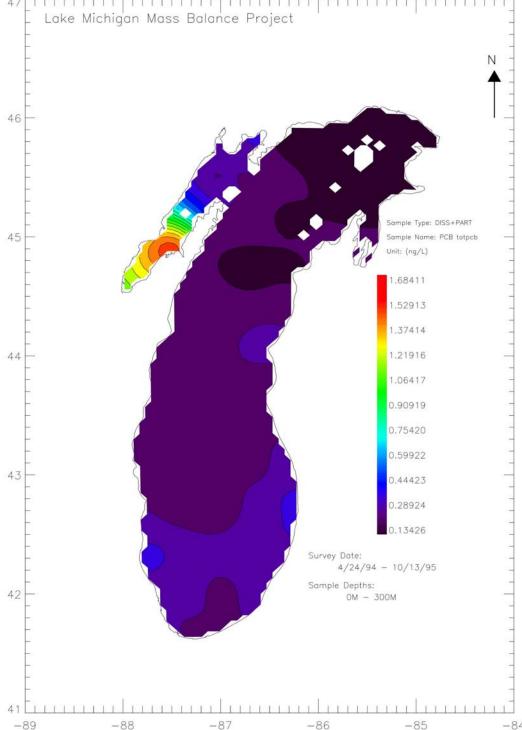


Figure 5-21. Concentrations of Total PCBs Measured in All LMMB Open-lake Samples



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5.3.2 Regional Considerations

Among the general trends evident in the contour plots for the particulate-phase results for PCBs 33, 118, and 180 (Figures 5-7 to 5-9, shown earlier) are the presence of "hot spots" in the upper reaches of Green Bay (on the western side of Lake Michigan). The apparent decrease in concentrations to the southwest of the hot spot, e.g., towards the head of Green Bay, is an artifact of the lack of a sampling station further up Green Bay (see Figure 5-1 for the locations of the two sampling stations in Green Bay). The lower reaches of the Fox River are a known source of sediments containing high levels of PCBs (see Chapter 4), and these hot spots in particulate PCB concentrations may be the result of resuspended sediments from the Fox River that are carried into Green Bay.

The PCB and *trans*-nonachlor results were examined to determine if there were any statistically significant differences between the northern and southern portions of Lake Michigan. For these comparisons, the data from the LMMB Study were divided at approximately 44° north latitude (see Figure 5-17 for the latitude). The dividing line at 44° N is not intended as a formal differentiation between hydrographic basins in the lake, and other means of differentiating the results from north to south could be considered. Rather, the line at 44° N yields approximately equal numbers of stations in each portion of the lake. The results from the two stations in Green Bay and the one station in Lake Huron were excluded from these comparisons. The stations in the lower portion of the lake include Stations 1 through 29, plus 310, 340, and 380. Stations 31 through 180 were in the northern portion of the lake.

The results of these comparisons for PCB congeners 33, 118, and 180, total PCBs and *trans*-nonachlor are shown in Table 5-17 for both the dissolved and particulate samples. There are statistical interactions between the effects of the cruise and the north/south division for some analytes, in which case, a comparison between the northern and southern stations cannot be made.

Table 5-17. Results of North/South Comparisons of Open-lake Concentrations of PCBs and trans-Nonachlor

Fraction/Analyte	Significant Difference Between North and South?	Probability	Direction		
Dissolved					
PCB 33	Yes	< 0.0001	South > North		
PCB 118	Interaction with cruise				
PCB 180	No	0.2326	NA		
Total PCBs	Yes	< 0.0001	South > North		
trans-Nonachlor	Yes	0.0043	South > North		
Particulate Particulate					
PCB 33	Interaction with cruise				
PCB 118	Yes	< 0.0001	South > North		
PCB 180	Yes	< 0.0001	South > North		
Total PCBs	Interaction with cruise				
trans-Nonachlor	Interaction with cruise				

NA = Not applicable

Of the 10 possible comparisons shown in Table 5-17, there were four interactions between the cruise and location. In five of the other six possible comparisons, there was a statistically significant difference, with concentrations in the southern portion of the lake greater than those in the northern portion of the lake.

Samples were collected from more than one depth at many of the stations during the periods when the lake was stratified. The choice of the depths of the samples was based on the position of the thermocline and other factors, but not a clear cutoff at a specific depth. As a result, it was possible to compare the concentrations of PCBs and *trans*-nonachlor between the samples collected near the surface and those collected below the thermocline. The results of these comparisons for PCB congeners 33, 118, and 180, total PCBs and *trans*-nonachlor are shown in Table 5-18 for both the dissolved and particulate samples, and for the results from the lake overall, those in the northern portion, and those in the southern portion of the lake. Generally speaking, most of the "shallow" samples were collected above 30 m, and all of the deep samples were collected below 30 m.

For the dissolved PCB results, the samples from the greater of the two depths at a station (e.g., the deeper samples) were significantly higher than the samples from the lesser of the two depths (e.g., the shallower samples) for all of the analytes except dissolved PCB 33. The differences between depths were consistent across the northern and southern stations, and for the lake overall.

For the particulate samples, the samples from the greater of the two depths at a station (e.g., the deeper samples) were significantly higher than the samples from the lesser of the two depths (e.g., the shallower samples) for all of the analytes except for particulate PCB 33 and *trans*-nonachlor in the northern portion of the lake. In both of those cases, the differences apparent in the results from the samples in the southern portion of the lake were sufficient to make the results different at depth in the lake overall.

These differences in concentrations with depth are consistent with the expected behavior of these hydrophobic contaminants. PCBs and *trans*-nonachlor are likely to be introduced into the open lake in a particulate form, either from atmospheric deposition or associated with particulate matter in tributary flows, or become associated with particulate matter in the lake through biological processes. As that particulate matter settles under the influence of gravity, the contaminants will settle too. In addition, based on the bathymetry of the Mackinac Channel between Lake Michigan and Lake Huron, the sill between the two lakes is at a depth of approximately 50 m. Therefore, even during winter months when the lakes are not thermally stratified, water below 50 m cannot flow out of Lake Michigan into Lake Huron. Although mixing of deeper water and surface water does occur and the mixed water may flow out of the lake, the deeper waters may retain their pollutant loads from historical sources long after the surface waters of the lake.

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Table 5-18. Results of Depth Comparisons of Open-lake Concentrations of PCBs and trans-Nonachlor

Fraction/Analyte/Location	Significant Difference between Shallow and Deep Results?	Probability	Direction
	Dissolved		•
PCB 33 - Overall	No	0.3615	NA
PCB 33 - South	No	0.1570	NA
PCB 33 - North	No	0.5513	NA
PCB 118 - Overall	Yes	<0.0001	Deep > Shallow
PCB 118 - South	Yes	<0.0001	Deep > Shallow
PCB 118 - North	Yes	<0.0001	Deep > Shallow
PCB 180 - Overall	Yes	0.0006	Deep > Shallow
PCB 180 - South	Yes	0.0245	Deep > Shallow
PCB 180 - North	Yes	0.0093	Deep > Shallow
Total PCB - Overall	Yes	< 0.0001	Deep > Shallow
Total PCB - South	Yes	< 0.0001	Deep > Shallow
Total PCB - North	Yes	0.0091	Deep > Shallow
trans-Nonachlor - Overall	Yes	< 0.0001	Deep > Shallow
trans-Nonachlor - South	Yes	< 0.0001	Deep > Shallow
trans-Nonachlor - North	Yes	< 0.0001	Deep > Shallow
	Particulate Particulate		
PCB 33 - Overall	Yes	<0.0001	Deep > Shallow
PCB 33 - South	Yes	<0.0001	Deep > Shallow
PCB 33 - North	No	0.3049	NA
PCB 118 - Overall	Yes	<0.0001	Deep > Shallow
PCB 118 - South	Yes	<0.0001	Deep > Shallow
PCB 118 - North	Yes	<0.0001	Deep > Shallow
PCB 180 - Overall	Yes	<0.0001	Deep > Shallow
PCB 180 - South	Yes	<0.0001	Deep > Shallow
PCB 180 - North	Yes	0.0013	Deep > Shallow
Total PCB - Overall	Yes	< 0.0001	Deep > Shallow
Total PCB - South	Yes	< 0.0001	Deep > Shallow
Total PCB - North	Yes	< 0.0001	Deep > Shallow
trans-Nonachlor - Overall	Yes	0.0003	Deep > Shallow
trans-Nonachlor - South	Yes	< 0.0001	Deep > Shallow
trans-Nonachlor - North	No	0.3507	NA

NA = Not applicable

5.3.3 Other Interpretations and Perspectives

As noted in various earlier sections of this report, there are limitations to the interpretations of the LMMB Study data presented here. Among the most basic considerations is the fact that this report has focused on providing the results for only three of the PCB congeners. The rationale for the choice of congeners is presented in Chapter 2. The interpretations suggested from the data for these three congeners may not apply to all other PCB congeners studied in the LMMB, and it would be advisable to examine the actual results for other congeners of interest before accepting the interpretations presented in this report.

The issues surrounding the evaluation of the blanks results in Section 5.2.3, and the impacts of the blanks on the interpretation of the field sample results cannot be overemphasized. As implemented in the LMMB Study, the sample collection and analysis procedures applied to PCBs and *trans*-nonachlor in open-lake waters represent a carefully crafted balance among practicality, affordability, and the size of the data set. Since the time that this study was conducted, more powerful analytical techniques such as high resolution GC/MS have been routinely applied to PCB congener analyses. However, the cost of such analyses would *severely* limit the number of samples that could be collected and analyzed the LMMB Study. While high resolution GC/MS may be able to better resolve some of the congeners, it would not necessarily better address the presence of PCBs in the blanks, except in instances where the contaminants are not actually PCBs, but had similar GC retention times.

Assessing temporal variation within the LMMB Study is hampered by the fact that not all stations were sampled on all cruises and that there are relatively few data from winter cruises. Comparisons between shallow and deep water samples suffer from similar problems, in that not all stations had samples at more than one depth. Therefore, the results for stations at different depths must be interpreted carefully.

Comparisons to historical data must consider not only the differences in the sizes of the various data sets (with the LMMB data set generally far larger than any other), but must also take into account significant differences in the sample collection and analysis procedures.

The concern about blanks for the LMMB data set is readily apparent in the data from Filkins *et al.* (1983) and although the investigators in the other two studies do not present similar blank results, it would be reasonable to assume that blanks would also have been a problem for those studies.

Finally, this report has used "contour" plots of PCB concentrations as a means of visually presenting parts of a large and complex data set. However, as noted earlier, there are limitations to those plots, particularly with regard to the identification of "hot spots" in Green Bay, as well as with the demarcation of PCB concentrations in the open lake when relatively few samples were collected.

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